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(54) PHOTSENSITIVE COMPOSITION FOR VOLUME HOLOGRAM RECORDING AND PHOTSENSITIVE MEDIUM FOR VOLUME HOLOGRAM RECORDING

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a photosensitive composition for volume hologram recording with large modulation quantity of the refractive index, for obtaining a volume hologram having controlled diffraction efficiency and half width as desired.
SOLUTION: The photosensitive composition for volume hologram recording comprises a binder resin, a photopolymerizable compound, a photoinitiator, and a sensitizer. The binder resin has 10,000 to 350,000 average molecular weight and $\geq 80^{\circ}\text{C}$ glass transition temperature. The volume hologram obtained by using the composition shows ≤ 20 nm half-value width of the diffraction spectrum and ≥ 0.03 refractive index modulation amount.

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(54) [発明の名称] 体積型ホログラム記録用感光性組成物および体積型ホログラム記録用感光性媒体

(57) 【要約】

【課題】 所望の回折効率、半値幅に制御された体積型ホログラムを得ることができる、回折率変動量の大きい体積型ホログラム記録用感光性組成物を提供する。

【解決手段】 バイソクシアリール樹脂、光重合性化合物、光重合開始剤、および増感剤を含んでなる体積型ホログラム記録用感光性組成物であって、前記バイソクシアリール樹脂の平均分子量が1万〜3.5万で、かつ、ガラス転移温度が80℃以上であり、この組成物を用いて得られる体積型ホログラムの回折スベクトルの半値幅が、20nm以下で、かつ、回折率変動量が0.03以上とする。

【選択図】 なし

【特許請求の範囲】

【請求項1】
 バイナリ樹脂、光重合性化合物、光重合開始剤、および増感剤を含んでなる体積型ホログラム記録用感光性組成物であって、
 前記バイナリ樹脂の平均分子量が1万～2.5万で、かつ、ガラス転移温度が80℃以上であり、
 この組成物を用いた感光性媒体を露光して体積型ホログラムを記録したときの、得られる体積型ホログラムの回折入射角の半値幅が、2.0 m以下で、かつ、屈折率変動量が0.03以上である、体積型ホログラム記録用感光性組成物。

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【請求項2】
 前記バイナリ樹脂が、アクリル系樹脂である、請求項1に記載の体積型ホログラム記録用感光性組成物。

【請求項3】
 バイナリ樹脂、光重合性化合物、光重合開始剤、および増感剤を含んでなる体積型ホログラム記録用感光性組成物であって、
 前記バイナリ樹脂の平均分子量が3.0万～1.0万で、かつ、ガラス転移温度が60℃以下であり、
 この組成物を用いた感光性媒体を露光して体積型ホログラムを記録したときの、得られる体積型ホログラムの回折入射角の半値幅が、2.0 m以下で、かつ、屈折率変動量が0.03以上である、体積型ホログラム記録用感光性組成物。

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【請求項4】
 前記バイナリ樹脂が、酢酸ニル系樹脂である、請求項3に記載の体積型ホログラム記録用感光性組成物。

【請求項5】
 バイナリ樹脂、光重合性化合物、光重合開始剤、および増感剤を含んでなる体積型ホログラム記録用感光性組成物であって、
 前記バイナリ樹脂の平均分子量が1万～2.6万で、かつ、ガラス転移温度が60℃以下であり、
 この組成物を用いた感光性媒体を露光して体積型ホログラムを記録したときの、得られる体積型ホログラムの回折入射角の半値幅が、2.5 m以下で、かつ、屈折率変動量が0.03以上である、体積型ホログラム記録用感光性組成物。

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【請求項6】
 前記バイナリ樹脂が、酢酸ニル系樹脂である、請求項5に記載の体積型ホログラム記録用感光性組成物。

【請求項7】
 請求項1～4のいずれか1項に記載の体積型ホログラム記録用感光性組成物からなる感光層が、透明基材上に設けられてなる体積型ホログラム記録用感光性媒体であって、
 体積型ホログラムを記録したときの、得られる体積型ホログラムの回折入射角の半値幅が、2.0 m以下で、かつ、屈折率変動量が0.03以上である、体積型ホログラム記録用感光性媒体。

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【請求項8】
 請求項5または6に記載の体積型ホログラム記録用感光性組成物からなる感光層が、透明基材上に設けられてなる体積型ホログラム記録用感光性媒体であって、
 体積型ホログラムを記録したときの、得られる体積型ホログラムの回折入射角の半値幅が、2.5 m以上で、かつ、屈折率変動量が0.03以上である、体積型ホログラム記録用感光性媒体。

【請求項9】
 請求項7に記載の体積型ホログラム記録用感光性媒体を用いた体積型ホログラムであって、回折入射角の半値幅が、2.0 m以下で、かつ、屈折率変動量が0.03以上である、体積型ホログラム。

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- 【請求項10】請求項8に記載の体積型ホログラム記録用感光性媒体を用いた体積型ホログラムであって、回折スベクトルの半値幅が、25nm以下で、かつ、屈折率変動量が0.03以上である、体積型ホログラム。
- 【発明の詳細な説明】
- 【技術分野】
- 【0001】体積型ホログラム用材料に関し、特に、屈折率変動 (Δn) が大きく、所望の回折効率、半値幅に制御された体積型ホログラムを得るための体積型ホログラム記録用感光性媒体および体積型ホログラム記録用感光性媒体に関する。
- 10 背景技術
- 【0002】体積型ホログラムは、物体を三次元で表現でき、高い回折効率、波長選択性を持つことと、波長が等しい物体光と参照光とを干渉させて、体積型ホログラム記録用材料に入射し、物体に関する三次元情報と材料内部に干渉縞として記録することにより作製されるものである。
- 【0003】その干渉縞は干渉光の明暗部分に対応した屈折率変動として記録される。また、体積型ホログラムの一つの特徴として、優れた波長選択性を有することが挙げられ、特定波長の光源 (人光光) に対して、特定の角度ないし波長の光のみを回折し再生できる。
- 【0004】近年、このような体積型ホログラムの特徴を利用して、体積型ホログラムを光学素子やフラットトップ等の分野に応用する試みが行われている。すなわち、再生回折光の中心波長や半値幅を制御することにより、再生光を特定のフロンプレルを有する光に変換することが行われている。
- 【0005】再生光の波長や半値幅を制御する方法として、例えば、特開平06-004015号公報に記載されているように光重合性化合物や可塑剤等を含有した溶媒にホログラム層を浸漬し、ホログラム再生波長を波長させることが開示されている (特許文献1)。また、特許第2602345号公報や特表平09-506441号公報には、光重合性化合物、可塑剤等からなる樹脂層をホログラム層に貼り合わせることで、乾式法により作製されるものの、ホログラム再生波長を波長させ、広帯域化することが開示されている (特許文献2および特許文献3)。
- 【0006】しかしながら、光重合性化合物、可塑剤等を含有した溶媒にホログラム層を浸漬する方法においては、溶媒を使用する湿式法であるため、湿式現象処理が煩雑で製造コストがかかるため量産には向きである。一方、光重合性化合物、可塑剤等からなる樹脂層をホログラム層に貼り合わせる方法においては、乾式法により作製されるものの、ホログラム記録用と別には波長制御を目的としたカラーチューニング層を設ける必要があるため、製造工程や材料等の観点から問題がある。
- 【特許文献1】特開平06-4015号公報
- 【特許文献2】特許第2602345号公報
- 【特許文献3】特表平09-506441号公報
- 【発明の概要】
- 【0007】本発明者は今般、ハイブリッドとして用いている樹脂のガラス転移温度および分子量を調整することにより、所望の回折効率および半値幅を有する体積型ホログラムが得られると知見を得た。本発明はかかる知見によるものである。
- 【0008】

【6000】

100

【 0 1 0 0 】

【 1 1 0 0 】

[0012]

【發明の具體的説明】

【0014】

【 0 0 1 5 】

【 9 1 0 0 】

 $\frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} \times \frac{1}{2}$

以下、本発明の体積型ホログラム記録用感光性組成物を構成する各成分について説明す

[8 1 0 0]

(1) バイナリー樹形図

本発明の体積型分子クラウエ記述性組成物を構成するハフマン一級脂は、第一の糖として、平均分子量が1万〜2.5万で、かつ、アッラ転移温度が80℃以上である。また、第二の糖としては、平均分子量が1万〜1.1万で、かつ、アッラ転移温度が80℃以上である。このような特性を有するハフマン一級脂としては、アッラ系樹脂が好ましく、特に、ポリ(メタ)アッラ樹脂が好適に用いられる。

また、本発明の第2の態様としてのバクテリオリンは、平均分子量が30万〜100万で、かつ、水へ溶解温度が60℃以下である。このような特性を有するバクテリオリンとして、酢酸・二乳酸脂が好ましく、特に、求り酢酸と二乳酸とこの加水分解物が好適に用いられる。

【 0 2 0 0 】

上記のような特性を有するハイブリッド樹脂を含んだ体積型ホログラム記録用感光性組成物を用いた体積型ホログラムにおいては、回折入射角の半値が、2.0°以下であつて、屈折率調整量が、0.03以上であり、回折効率の悪いホログラムとして光學的に適用できる。すなわち、回折効率が高く、かつ半値幅が小さく波長選択性に優れたもの、特定波長の光を特定方向に効率的に回折でき、回折光学素子や波長選択フィルター等の応用に好適である。

【 0 0 2 1 】

また、本発明の第三の態様として、パルマー油の平均分子量が1万～2.6万で、かつ、水不溶性の第三の成分が60℃以下である。好ましい態様としては、平均分子量が1万～2.5万で、かつ、水不溶性の第三の成分が60℃以上である。このような特性を有するパルマー油としては、酢酸に二ル系樹脂が好ましく、特に、求引酢酸に二ル又はその加水分解物が好適に用いられる。【0022】

上記の如く

光性組成物を用いた液晶調製が、同折入ハタチにおいて、0.3以上であれば、ガラスアハタチの半偏幅が、2.5 nm 求される分厚に好適に用いることができる。すなわち、半偏幅が大きく、かつ波長の波長と光を有効に利用できるため、P O Pやポリメチルメタクリレート等、視認性がよく高く要求される分野への応用に好適である。

[0023]

なす、本発

法 (GPC) により測定し、 β 因子を分析し換算した値である。また、 β 因子変換温度は、一般に、動的粘弾性測定、示差熱分析、ないし公知の手法により測定できるが、本発明においては、動的粘弾性測定における損失正値が最大値をとる温度を当該樹脂の β 因子変換温度としたものである。なお、 β 因子変換温度は、Kogalnik の下記理論式 (Bell Syst. Tech. J., 48, 2909 (1969) に記載) より算出されるものである。

$$(\theta \circ \gamma / p(u, v)) = \gamma(u, v) = u$$

01

02

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05

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本発明の体積型ホログラム記録用感光性組成物を構成する光重合性化合物としては、光ラジカル重合性化合物、光カチオン重合性化合物、ないし光二量体化化合物等が挙げられ、これら光重合性化合物の含有量は、バニリン樹脂100重量部に対して10～1000重量部、好ましくは10～200重量部である。【0029】

【0055】

実施例 1

下記に示す材料を用いて、体積型ホログラム記録用感光性組成物溶液を調整した。

【0056】

求りメチルメタクリレート

(求りメチル換算重量平均分子量：1万5千)

100重量部

1, 6-ヘキサメチルシロキシシランエーテル

70重量部

(チガセケムチックス製EX-212)

シマダエチルメチルシロキシシリレート

80重量部

(大阪ガス製BPEFA)

シマダエチルメチルシロキシシリレート

5重量部

2, 5-ビス-(4-ジエチルフェニル)シクロペンタジ

1重量部

30重量部

メチルエチルケトン

30重量部

上記の調整した溶液を、38μmの求りエチルシロキシシリレート(PET)フィルム(東レ製ミラーT-6)上にバキューターを使用して、乾燥膜厚10μmとなるように塗布し、体積型ホログラム記録用感光性媒体を制作した。

露光側をミラーにラミネートし、PET側から532nmレーザ光を60mJ/cm²入射して、体積型ホログラムを記録した。

【0057】

次いで、加熱、紫外線全面照射により感光層を固定し、体積型ホログラムを得た。

得られた体積ホログラムについて、分光光度計(島津製作所製UVPC-3100)の透過率測定を行い、屈折率差調整(Δn)、回折効率、および半値幅の算出を行った。

【0058】

なお、回折効率ηは、得られた透過スペクトルのピーク透過率をT_p、ベースラインの透過率をT_bとして、下記式、

$$\eta = (T_p - T_b) / T_p$$

により算出し、半値幅(T_{1/2})は、透過率のピーク値(T_p)とベースライン透過率(T_b)の差の1/2の値を下記式、

$$T_{1/2} = (T_p - T_b) / 2$$

により算出し、T_{1/2}時の透過スペクトル(透過波長)幅を半値幅とした。得られた、回折効率および半値幅の値を用いて、上記のKogelnik理論式によりΔnを算出した。

【0059】

実施例 2

下記に示す材料を用いて、体積型ホログラム記録用感光性組成物溶液を調整した。

100重量部

1, 6-ヘキサメチルシロキシシランエーテル

70重量部

(チガセケムチックス製EX-212)

シマダエチルメチルシロキシシリレート

80重量部

(大阪ガス製BPEFA)

シマダエチルメチルシロキシシリレート

5重量部

2, 5-ビス-(4-ジエチルフェニル)シクロペンタジ

1重量部

30重量部

メチルエチルケトン

30重量部

上記の調整した溶液を、38μmの求りエチルシロキシシリレート(PET)フィルム(東レ製ミラーT-6)上にバキューターを使用して、乾燥膜厚10μmとなるように塗布し、体積型ホログラム記録用感光性媒体を制作した。

露光側をミラーにラミネートし、PET側から532nmレーザ光を60mJ/cm²入射して、体積型ホログラムを記録した。

【0060】

実施例 3

下記に示す材料を用いて、体積型ホログラム記録用感光性組成物溶液を調整した。

求りメチルメタクリレート

(求りメチル換算重量平均分子量：1万5千)

100重量部

1, 6-ヘキサメチルシロキシシランエーテル

70重量部

(チガセケムチックス製EX-212)

シマダエチルメチルシロキシシリレート

80重量部

(大阪ガス製BPEFA)

シマダエチルメチルシロキシシリレート

5重量部

2, 5-ビス-(4-ジエチルフェニル)シクロペンタジ

1重量部

30重量部

メチルエチルケトン

30重量部

上記の調整した溶液を、38μmの求りエチルシロキシシリレート(PET)フィルム(東レ製ミラーT-6)上にバキューターを使用して、乾燥膜厚10μmとなるように塗布し、体積型ホログラム記録用感光性組成物溶液を調整した。

露光側をミラーにラミネートし、PET側から532nmレーザ光を60mJ/cm²入射して、体積型ホログラムを記録した。

[illegible]

実施例 7

【0064】

実施例 1 と同様にして、体積型ホログラム作製し、諸物性についての測定を行った。

下記に示す材料を用いて、体積型ホログラム記録用感光性組成物溶液を調整した。

求り酢酸ビニル
(求りスチレン換算重量平均分子量：10万)
1, 6-ヘキサメチレンジオールジグリシジルエーテル
(オガセケムスチックス製 EX-212)
ジエノキシエタノールジオレシジフクリレート
(大阪ガス製 B P E F A)
ジブチルヨードニウム塩 (ローチケイ製、P 12074)
2, 5-エース- (4-ジエチルフェニルペンシチン) シクロペンタノ
1-ブタノール
メチルエチルケトン
30 重量部

10

70 重量部
80 重量部
5 重量部
1 重量部
30 重量部
30 重量部

実施例 8

【0065】

実施例 1 と同様にして、体積型ホログラム作製し、諸物性についての測定を行った。

下記に示す材料を用いて、体積型ホログラム記録用感光性組成物溶液を調整した。

求り酢酸ビニル
(求りスチレン換算重量平均分子量：2.6万)
1, 6-ヘキサメチレンジオールジグリシジルエーテル
(オガセケムスチックス製 EX-212)
ジエノキシエタノールジオレシジフクリレート
(大阪ガス製 B P E F A)
ジブチルヨードニウム塩 (ローチケイ製、P 12074)
2, 5-エース- (4-ジエチルフェニルペンシチン) シクロペンタノ
1-ブタノール
メチルエチルケトン
30 重量部

20

70 重量部
80 重量部
5 重量部
1 重量部
30 重量部
30 重量部

実施例 9

【0066】

実施例 1 と同様にして、体積型ホログラム作製し、諸物性についての測定を行った。

下記に示す材料を用いて、体積型ホログラム記録用感光性組成物溶液を調整した。

求り酢酸ビニル
(求りスチレン換算重量平均分子量：17万)
1, 6-ヘキサメチレンジオールジグリシジルエーテル
(オガセケムスチックス製 EX-212)
ジエノキシエタノールジオレシジフクリレート
(大阪ガス製 B P E F A)
ジブチルヨードニウム塩 (ローチケイ製、P 12074)
2, 5-エース- (4-ジエチルフェニルペンシチン) シクロペンタノ
1-ブタノール
メチルエチルケトン
30 重量部

40

70 重量部
80 重量部
5 重量部
1 重量部
30 重量部
30 重量部

実施例 10

【0067】

実施例 1 と同様にして、体積型ホログラム作製し、諸物性についての測定を行った。

下記に示す材料を用いて、体積型ホログラム記録用感光性組成物溶液を調整した。

求り酢酸ビニル
(求りスチレン換算重量平均分子量：10万)
1, 6-ヘキサメチレンジオールジグリシジルエーテル

50

30 重量部

(ナリセケムチンアクリル酸 E X-212)
 シンエノキシエタノールモノレブソジアクリレート
 (大阪ガス製 B P E F A)
 シアリールエポキシ樹脂 (ロークイア製、P12074)
 2, 5-エス- (4-エチルフェニルモノレブソジアクリレート) シクロペンタノ
 1-ブチロール
 シタルエチルクト
 実施例 1 と同様に、体積型ホログラム作製し、諸物性についての測定を行った。

【0068】

下記に示す材料を用いて、体積型ホログラム記録用感光性組成物溶液を調製した。

ホリマチルメタクリレート
 (ホリマチル換算重量平均分子量：1.2万)
 1, 6-ヘキサメチレンジオールジアクリレート
 (ナリセケムチンアクリル酸 E X-212)
 シンエノキシエタノールモノレブソジアクリレート
 (大阪ガス製 B P E F A)
 2-メタクリルホリマチルモノレブソジアクリレート (アルドリッチ製)
 2, 5-エス- (4-エチルフェニルモノレブソジアクリレート) シクロペンタノ
 1-ブチロール
 シタルエチルクト
 3 0 重量部
 8 0 重量部
 5 重量部
 5 重量部
 1 重量部
 7 0 重量部
 1 0 0 重量部

表 1 に、用いたバインダー樹脂の材料物性および体積ホログラムの評価結果を示す。

【表 1】

表 1 バインダー樹脂の材料物性および体積ホログラムの評価結果

評価	バインダー樹脂		分子重*	Δn	回折効率 (%)	半値幅 (nm)
	樹脂	Tg (°C)				
実施例 1	ホリマチルメタクリレート	98	15,000	0.031	60	20
実施例 2	ホリマチルメタクリレート	105	70,000	0.035	90	18
実施例 3	ホリマチルメタクリレート	110	93,000	0.034	93	17
実施例 4	ホリマチルメタクリレート	114	120,000	0.031	95	15
実施例 5	ホリマチルメタクリレート	45	500,000	0.032	80	18
実施例 6	ホリマチルメタクリレート	43	83,000	0.050	70	30
実施例 7	ホリマチルメタクリレート	45	100,000	0.047	80	28
実施例 8	ホリマチルメタクリレート	30	260,000	0.044	76	25
実施例 9	ホリマチルメタクリレート	45	170,000	0.050	84	27
実施例 10	ホリマチルメタクリレート	~24	100,000	0.065	74	38
比較例 1	ホリマチルメタクリレート	122	300,000	0.029	98	13.6

* ホリマチル換算重量平均分子量

40

30

20

10

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Fターム(参考) 2K008 MA04 DD13 FF17

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- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[Field of the Invention]

[0001]

About the charge of volume type hologram material, especially, refractive index modulation (δn) is large and it is related with the photosensitive composition for volume type hologram record for obtaining the volume type hologram controlled by desired diffraction efficiency and half breadth, and the photosensitive medium for volume type hologram record.

[Background of the Invention]

[0002]

The volume type hologram can express an object by three dimensions, and since having high diffraction efficiency and wavelength selectivity and advanced production technology are required, it is broadly used as a design use, a security use, and an optical element use. This volume type hologram has high coherence nature (coherence), wavelength makes equal object light and reference beam interfere, and enters into volume type hologram writing materials, and it is produced by recording the three dimensional information about an object on the inside of material as an interference fringe.

[0003]

This interference fringe is recorded as refractive index modulation corresponding to the light-and-darkness portion of the interference light. It is mentioned, and to the light source (input light) of a specified wavelength, having the outstanding wavelength selectivity as one feature of a volume type hologram diffracts only the light of a specific angle thru/or wavelength, and it can be reproduced.

[0004]

In recent years, the trial which applies a volume type hologram to fields, such as an optical element and graphic arts, is made using the feature of such a volume type hologram. That is,

changing regenerated light into the light which has a specific profile is performed by controlling the center wavelength and half breadth of the reproduction diffracted light.

[0005]

As a method of controlling the wavelength and half breadth of regenerated light, a hologram layer is immersed in the solvent containing a photopolymerization nature compound, a plasticizer, etc., for example as indicated to JP,06-004015,A, and changing a hologram reproducing wave length is indicated (patent documents 1). Changing a hologram reproducing wave length and broadband-izing it is indicated by pasting together to a hologram layer the resin layer which becomes the patent No. 2602345 gazette and the Patent Publication Heisei No. 506441 [09 to] gazette from a photopolymerization nature compound, a plasticizer, etc. (patent documents 2 and patent documents 3).

[0006]

However, in the method of immersing a hologram layer in the solvent containing a photopolymerization nature compound, a plasticizer, etc., since it is the wet process which uses a solvent, wet-developing processing is complicated, and since a manufacturing cost is applied, it is unsuitable for mass production. In the method of on the other hand pasting together to a hologram layer the resin layer which consists of a photopolymerization nature compound, a plasticizer, etc., although produced by a dry method, since it is necessary to provide the color tuning layer aiming at wavelength control apart from a hologram recording layer, there is a problem from a viewpoint of a manufacturing process, material, etc.

[Patent documents 1] JP,06-4015,A

[Patent documents 2] The patent No. 2602345 gazette

[Patent documents 3] The Patent Publication Heisei No. 506441 [09 to] gazette

[0007]

This invention persons acquired knowledge that the volume type hologram which has desired diffraction efficiency and half breadth is obtained by adjusting the glass transition temperature and the molecular weight of the resin used as a binder this time. This invention is based on this knowledge.

[0008]

That is, the purpose of this invention is the volume type hologram controlled by desired diffraction efficiency and half breadth, and there is in providing the photosensitive composition for volume type hologram record and the photosensitive medium for volume type hologram record which can obtain a volume type hologram with the large amount of refractive index modulation.

[0009]

The photosensitive composition for volume type hologram record of this invention is a

photosensitive composition for volume type hologram record containing binder resin, a photopolymerization nature compound, a photopolymerization initiator, and a sensitizer, The average molecular weights of said binder resin are 10,000-250,000, and glass transition temperature is not less than 80 °C. The half breadth of the diffraction spectrum of a volume type hologram in which it is obtained when the photosensitive medium using this constituent is exposed and a volume type hologram is recorded is 20 nm or less, and the amount of refractive index modulation is 0.03 or more. As for the above-mentioned binder resin, it is preferred that it is acrylic resin.

[0010]

The photosensitive composition for volume type hologram record as another mode of this invention, it is a photosensitive composition for volume type hologram record containing binder resin, a photopolymerization nature compound, a photopolymerization initiator, and a sensitizer, and the average molecular weights of said binder resin are 300,000-1 million, and glass transition temperature is 60 °C or less. The half breadth of the diffraction spectrum of a volume type hologram in which it is obtained when the photosensitive medium using this constituent is exposed and a volume type hologram is recorded is 20 nm or less, and the amount of refractive index modulation is 0.03 or more. As for the above-mentioned binder resin, it is preferred that it is vinyl acetate system resin.

[0011]

The photosensitive composition for volume type hologram record as another mode of this invention, it is a photosensitive composition for volume type hologram record containing binder resin, a photopolymerization nature compound, a photopolymerization initiator, and a sensitizer, and the average molecular weights of said binder resin are 10,000-260,000, and glass transition temperature is 60 °C or less. The half breadth of the diffraction spectrum of a volume type hologram in which it is obtained when the photosensitive medium using this constituent is exposed and a volume type hologram is recorded is not less than 25 nm, and the amount of refractive index modulation is 0.03 or more.

[0012]

As for the above-mentioned binder resin, it is preferred that it is vinyl acetate system resin. By using such a photosensitive composition, it is the volume type hologram controlled by desired diffraction efficiency and half breadth, and a volume type hologram with the large amount of refractive index modulation can be obtained.

[Detailed Description of the Invention]

[0013]

It explains in more detail about the photosensitive medium for volume type hologram record

using the photosensitive composition for volume type hologram record and this photosensitive composition of this invention.

[0014]

1. Photosensitive composition for volume type hologram record

The photosensitive composition for volume type hologram record provided by this invention consists of binder resin, a photopolymerization nature compound, a photopolymerization initiator, and a sensitizer to which sensitization of the sensitivity to the visible-laser-beams wavelength of said photopolymerization initiator is carried out.

When the molecular weight and glass transition point use the resin which has a predetermined range as this binder resin, the volume hologram which has desired diffraction efficiency and a diffraction spectrum of half breadth can be obtained.

[0015]

For example, the volume type hologram which has a high profile with small half breadth of a spectrum has useful diffraction efficiency as a recording material for optics. In the volume type hologram which, on the other hand, has a profile with large half breadth, a hologram image is bright and useful to graphic arts etc.

[0016]

Thus, the material physical properties of the binder resin to be used are controlled by this invention.

Therefore, it finds out that the volume type hologram which has a desired diffraction-spectrum profile can be obtained.

[0017]

Hereafter, each ingredient which constitutes the photosensitive composition for volume type hologram record of this invention is explained.

[0018]

(1) Binder resin

As the first mode, average molecular weights are 10,000-250,000, and the binder resin in which constitutes the photosensitive composition for volume type hologram record of this invention is not less than 80 ** in glass transition temperature. As a desirable mode, average molecular weights are 10,000-110,000, and glass transition temperature is not less than 80 **. As binder resin which has such the characteristic, acrylic resin is preferred and poly(meta) acrylic ester or its partial hydrolyzate is used especially suitably.

[0019]

Average molecular weights are 300,000-1 million, and binder resin as the 2nd mode of this invention is 60 ** or less in glass transition temperature. As binder resin which has such the

characteristic, vinyl acetate system resin is preferred and polyvinyl acetate or its hydrolyzate is used especially suitably.

[0020]

In the volume type hologram using the photosensitive composition for volume type hologram record containing the binder resin which has the above physical properties, The half breadth of a diffraction spectrum is 20 nm or less, and the amount of refractive index modulation is 0.03 or more, and it can apply to an optical application as a hologram with high diffraction efficiency. That is, since diffraction efficiency excels [half breadth] in wavelength selectivity small highly, suitable for the application to a diffraction optical element, a wavelength selection filter, etc.

[0021]

As the third mode of this invention, the average molecular weights of binder resin are 10,000-260,000, and glass transition temperature is 60 ° or less. As a desirable mode, average molecular weights are 10,000-250,000, and glass transition temperature is not less than 60 °. As binder resin which has such the characteristic, vinyl acetate system resin is preferred and polyvinyl acetate or its hydrolyzate is used especially suitably.

[0022]

In the volume type hologram using the photosensitive composition for volume type hologram record containing the binder resin which has the above material physical properties, The half breadth of a diffraction spectrum is not less than 25 nm, and the amount of refractive index modulation is 0.03 or more, and it can use conveniently for the field as which luminositess, such as graphic arts, are required. That is, since the light of wavelength with it can be used effectively and a picture becomes bright, visibility is suitable for POP, premium goods, etc. to the application to the field demanded more highly. [large and half breadth and] [wide range]

[0023]

An "average molecular weight" [which is used for this invention] The becoming term is the value which meant weight average molecular weight, measured by gel filtration technique (GPC), and carried out polystyrene conversion. Generally, although glass transition temperature can be measured with dynamic viscoelasticity measurement, differential thermal analysis, or a publicly known technique, in this invention, it makes temperature to which the loss tangent in dynamic viscoelasticity measurement takes the maximum the glass transition temperature of the resin concerned. The amount of refractive index modulation (delta) is said hereafter) is computed from the following theoretical formula (it indicates to Bell Syst. Tech. J., 48, and 2909 (1969)) of Kogelnik.

$$\text{Eta}=\tanh^2(\text{pi}(\text{delta})/\text{lambda}\text{d}\cos\text{theta}_0)$$

(Here, as for diffraction efficiency and d, a record laser wavelength and theta₀ of sensitized

material thickness and lambda are [eta] the degrees of incidence angle to the inside of the sensitized material of recording laser light.)

In this invention, it cannot be overemphasized that not ** limited to the above-mentioned binder resin but resin possessing a predetermined property value can be used. Specifically Polyvinyl alcohol or its partial acetalization thing, T raceety cellulose, polyisoprene, polybutadiene, polychloroprene, Silicone rubber, polystyrene, a polyvinyl butyral, polychloroprene, Polyvinyl chloride, polyarylate, chlorinated polyethylene, chlorinated polypropylene, Poly-N-vinylcarbazole or its derivative, Poly N-vinyl pyrrolidone, or its derivative, The copolymer or its half ester of polyarylate, styrene, and a maleic anhydride, Acrylic acid, acrylic ester, methacrylic acid, methacrylic acid ester, Those mixtures, such as a copolymer which uses at least one of the copolymerizable monomer groups, such as acrylamide, acrylic nitril, ethylene, propylene, VCM/PVC, and vinyl acetate, as a polymerization component, are used. The monomer containing the hardenablely functional group in which heat curing or photo-curing is possible can be used as a copolymer component. Thus, by using a hardenablely monomer, film strength improves and heat resistance and mechanical strength improve.

[0024]

Oligomer type hardening resin can also be used as binder resin. For example, various phenolic compounds, such as bisphenol A, the bisphenol S, novolac, o-cresolnovolak, and p-alkylphenol novolac, the epoxy compound generated by the condensation reaction with epichlorohydrin, etc. are mentioned.

[0025]

Organic-inorganic matter hybrid resin using a sol gel reaction can also be used as binder resin. As that of organic - inorganic matter hybrid polymer, the copolymer of the organic metallic compound and vinyl monomer which are expressed with a following general formula (1) and which have a polymerization nature group is mentioned, for example.



(Here, M is metal, such as Si, Ti, Zr, Zn, In, Sn, aluminum, or Se, R is a vinyl group of the carbon numbers 1-10, or (meta) an acrylyl group, R' is an alkyl group of the carbon numbers 1-10, and m+n expresses the valence of the metal M.)

As an organic metallic compound in the case of using Si as metal, For example, vinyltriethoxysilane, vinyltrimetoxysilane, BINIRUTORI butoxysilane, Although a vinyl triaryloxysilane, a vinyltetraethoxysilane, a vinyl tetramethoxy silane,

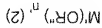
acryloxypropyltrimethoxysilane, methacryloxy propyl trimethoxysilane, etc. are mentioned, it is not limited to these.

[0026]

Although acrylic acid, acrylic ester, methacrylic acid, and methacrylic acid ester are mentioned as a vinyl monomer, for example, it is not limited to these.

[0027]

In order to enlarge refractive index difference of binder resin and a photopolymerization nature compound, the organic metallic compound expressed with a following general formula (2) can also be added in a constituent.



(Here, Mⁿ is metal, such as Ti, Zr, Zn, In, Sn, aluminum, or Se, Rⁿ is an alkyl group of the carbon numbers 1-10, and n⁺ expresses the valence of metal Mⁿ.)

putting under existence of water thru/or an acid catalyst, if the above-mentioned organic metallic compound is added -- sol -- by a --*** reaction, since above-mentioned binder resin and network structure are formed, it not only raises the refractive index of binder resin, but it can also raise the toughness of a film when it is considered as a hologram recording medium, and heat resistance. In order to raise refractive index difference with a photopolymerization nature compound, it is preferred to use the organic metallic compound combination which has metal with a refractive index high as much as possible (Mⁿ).

[0028]

(2) Photopolymerization nature compound

As a photopolymerization nature compound which constitutes the photosensitive composition for volume type hologram record of this invention, an optical radical polymerization nature compound, an optical cationic polymerization nature compound, or an optical Ni quantification nature compound is mentioned. As content of these photopolymerization nature compound, it is ten to 200 weight section preferably ten to 1000 weight section to binder resin 100 weight section.

[0029]

The compound which has an ethylenic unsaturated double bond in which at least one addition condensation is possible as an optical radical polymerization nature compound is mentioned. For example, unsaturated carboxylic acid and its salt, ester of unsaturated carboxylic acid and an aliphatic polyalcohol compound, and the amide bond thing of unsaturated carboxylic acid and an aliphatic polyamine compound are mentioned. The monomer of ester of an aliphatic polyalcohol compound and unsaturated carboxylic acid is mentioned as an example. As acrylic ester, ethylene glycol diacrylate, triethylene glycol diacrylate, 1,3-butanediol diacrylate, tetramethylene glycol diacrylate, Propylene glycol diacrylate, neopentyl glycol diacrylate, Trimethylolpropane triacrylate, TORIMETCHI roll pro panty (acryloyloxypropyl) ether, Trimethylol triacrylate, hexanediol diacrylate, 1,4-cyclohexanediol diacrylate, tetraethylene glycol diacrylate, pentaerythritol diacrylate -- and, [pentaerythritol doria] Pentaerythritol tetraacrylate, dipentaerythritol diacrylate, Dipentaerythritol triacrylate, dipentaerythritol tetraacrylate, dipentaerythritol hexaacrylate -- and, [sorbitol doria] Sorbitol tetraacrylate, sorbitol pentaacrylate, sorbitol hexa acrylate, Tori (acryloyloxyethyl) isocyanurate, polyester-

acrylates oligomer, 2-phenoxy ethyl acrylate, 2-phenoxy ethyl acrylate, Phenol ethoxy rate monoacrylate, 2-(p-chlorophenoxy) ethyl acrylate, p-chlorophenyl acrylate, phenyl acrylate, 2-phenylethyl acrylate, The ether (2-acrylic oxyethyl) of bisphenol A, the ethoxylated bisphenol A diacrylate, 2-(1-naphthyl)oxy ethyl acrylate, o-biphenyl acrylate, o-biphenyl acrylate, A 9,9-bis(4-acryloxy diethoxyphenyl)(fluorene, A 9,9-bis(4-acryloxy TORIE TOKISHI phenyl)(fluorene, A 9,9-bis(4-acryloxy dipropoxyphenyl)(fluorene, A 9,9-bis(4-acryloxy ethoxy-3-methylphenyl) fluorene, A 9,9-bis(4-acryloxy ethoxy-3-ethylphenyl)(fluorene, A 9,9-bis(4-acryloxy ethoxy-3,5-dimethyl)(fluorene, etc. are illustrated.

[0030]

The sulfur content acrylic compound currently indicated by JP,61-72748,A can also be used. For example, 4,4'-bis(beta-acryloyloxyethyl thio)diphenylsulfone, 4,4'-bis(beta-acryloyloxyethyl thio)diphenyl ketone, Although 4,4'-bis(beta-acryloyloxyethyl thio)-3,3',5,5'-tetrabromo diphenyl thio)diphenyl ketone, Although 4,4'-bis(beta-acryloyloxyethyl thio)-3,3',5,5'-tetrabromo diphenyl ketone and 2,4-bis(beta-acryloyloxyethyl thio)diphenyl ketone are mentioned, it is not limited to these.

[0031]

As methacrylic acid ester, the compound in which "acrylate" turns into "methacrylate" among the above-mentioned acrylic ester compound names, "acryloxy" turns into "meta-KURIROROKISHI", and "acryloyl" turns into "methacryloyl one" is illustrated as an example.

[0032]

As an optical cationic polymerization nature compound, the cyclic ether, thioether, and vinyl ether which are represented by an epoxy ring and the oxetane ring are mentioned. An epoxy ring content compound is mentioned as an example. Polyalkylene glycol diglycidyl ether, bisphenol A diglycidyl ether, glycerol triglycidyl ether and a jig -- a lycee -- roll triglycidyl ether. Although diglycidyl hexahydro phthalate, trimethylolpropane diglycidyl ether, allyl glycidyl ether, phenyl glycidyl ether, cyclohexane oxide, etc. are illustrated, it is not limited to these.

[0033]

The compound which embellished the metal particle surface with the reactant group can also be used, for example, Ti with a refractive index high as metal particles, Zr, Zn, In, Sn, etc. are illustrated. As a gestat of photopolymerization, the above-mentioned radical polymerization and cationic polymerization are mentioned. It can introduce by the ethylenic unsaturated double bond in which at least one addition condensation is possible being mentioned as a functional group in which an optical radical polymerization is possible, for example, processing a surface of metal by an ethylenic unsaturated double bond content silane coupling agent etc. As an ethylenic unsaturated double bond content silane coupling agent, although the above-mentioned vinylsilane, an acryloyl (meta) silane, etc. can be used, it is not limited to these.

[0034]

It can introduce by the cyclic ether, thioether, and vinyl ether which are represented by an

epoxy ring and the oxetane ring being mentioned as a functional group in which optical cationic polymerization is possible, for example, processing a surface of metal by an epoxy ring content silane coupling agent. As an epoxy ring content silane coupling agent, although beta-(3, 4-epoxycyclohexyl) ethyltrimethoxysilane, gamma-glycidioxypropyltrimethoxysilane, etc. are illustrated, it is not limited to these.

[0035]

(3) Photopolymerization initiator

As a polymerization initiator which constitutes the photosensitive composition for volume type hologram record of this invention, an optical radical polymerization initiator thru or an optical cationic initiator can be used. The content of these photopolymerization initiators is five to 15 weight section preferably 0.1 to 20 weight section to binder resin 100 weight section.

[0036]

As an optical radical polymerization initiator, an imidazole derivative, a screw imidazole derivative, N-aryl glycine derivative, an organic azide compound, titanocene, an aluminate complex, organic peroxide, N-alkoxy pyridinium salt, a thioxan ion derivative, etc. are mentioned, and also specifically, 1,3-*l*l (1-butylidioxycarbonyl) benzophenone, 3,3',4,4'-tetakis (1,4,5-triphenyl)imidazole, 2,2-dimethoxy-1,2-diphenylethan 1-one (trade name IRGACURE 651, made in Tiba Specialty Chemicals), 1-hydroxy-cyclohexyl-p-phenyl-ketone (trade name IRGACURE 184, made in Tiba Specialty Chemicals), 2-benzyl-2-dimethylamino 1-(4-morpholinophenyl)-Butanone-1 (trade name IRGACURE 369, made in Tiba Specialty Chemicals), Although bis(2,4-cyclopentadiene 1-yl)-bis(2,6-difluoro-3-(1H-pyrrol 1-yl)-phenyl)titanium (trade name IRGACURE 784, made in Tiba Specialty Chemicals) etc. are mentioned, it is not limited to these.

[0037]

As an optical cationic initiator, sulfonic ester, imide sulfonate, Dialkyl 4-hydroxysulfonium salt, aryl sulfone acid-p-nitrobenzyl ester, Although a silanol aluminum complex, iron (eta(eta-6-benzene)5-cyclopentadienyl) (II), etc. are illustrated and also benzoin tosylate, 2,5-dinitrobenzyl tosylate, N-TOSHIFFUTARU acid imide, etc. are specifically mentioned, it is not limited to these.

[0038]

As what is used also as an optical cationic initiator also as an optical radical polymerization initiator, Aromatic iodonium salt, aromatic sulfonium salt, aromatic diazonium salt, aromatic phosphonium salt, a triazine compound, an iron arene complex, etc. are illustrated, and also specifically, Diphenyliodonium, ditolyl iodonium, bis(p-tert-butylphenyl)iodonium, Chloride of iodonium, such as bis(p-chlorophenyl)iodonium, Iodonium salt, such as bromide, Howe fluoride salt, a hexafluorophosphate salt, and a hexafluoroantimonate salt, Triphenylsulfonium, 4-tert-

butyl triphenylsulfonium, Chloride of sulfonium, such as tris (4-methylphenyl) sulfonium, sulfonium salt, such as bromide, Howe fluoride salt, a hexafluorophosphate salt, and a hexafluoroantimonate salt, 2,4,6-tris (trichloromethyl)-1,3,5-triazine, 2-phenyl-4,6-bis (trichloromethyl)-1,3,5-triazine, Although 2, such as 2-methyl-4,6-bis(trichloromethyl)-1,3,5-triazine, 4, 6-substitution-1, 3, and 5-triazine compound is mentioned, it is not limited to these.

[0039]

As for a photopolymerization initiator, it is preferred that decomposition treatment is carried out after hologram recording from a viewpoint of stabilization of the recorded hologram.

[0040]

(4) Sensitizer

The sensitizer which constitutes the photosensitive composition for volume type hologram record of this invention bears the role to which sensitization of the sensitivity to the recording light of the above-mentioned photopolymerization is carried out. Specifically Thio pyrylium salt dye, merocyanine system coloring matter, quinoline dye, Styrylquinoline dye, ketocoumarin dye, thioxanthene dye, a xanthene dye, oxonol dye, cyanine dye, rhodamine dye, pyrylium salt dye, cyclopentanone system coloring matter, cyclohexanone series coloring matter, etc. are illustrated. As an example of cyanine and merocyanine system coloring matter, 3',3'-dicarboxyethyl-2,2'-thiocyaninebromide, 1'-carboxymethyl 2,2'-kino cyaninebromide, 1,3'-diethyl-2,2'-kino thia cyaninebromide, 3-ethyl-5-[3-ethyl-2(3H)-benzothia ZORIRIDEN] ethylidene-2-thioxo-4-oxazolidine, etc. are mentioned, As an example of a coumarin and ketocoumarin dye, A 3-(2'-benzimidazole)-7-diethylamino coumarin, Although a 3,3'-carbonyl screw (7-diethylamino coumarin), a 3,3'-carbonyl bisque marine **3,3'-carbonyl screw (5,7-dimethoxycoumarin), a 3,3'-carbonyl screw (7-acetoxycoumarin), etc. are mentioned, it is not limited to these.

[0041]

As for a visible photosensitizer, when high transparency like an optical element is required, what becomes colorlessness by decomposition etc. is preferred at the time of the post process after hologram recording, heating, or UV irradiation.

[0042]

The content of this sensitizer is 0.01 to 3 weight section preferably 0.01 to 10 weight section to binder resin 100 weight section.

[0043]

It is made to dissolve in a solvent and these photosensitive compositions for volume type hologram record are used as coating liquid. As a solvent, acetone, methyl ethyl ketone, methyl isobutyl ketone, Cyclohexanone, benzene, toluene, xylene, chlorobenzene, A tetrahydrofuran, methyl cellosolve, ethylcellosolve, methyl-cellosolve acetate, Although **, such as ethylcellosolve acetate, ethyl acetate, 1,4-dioxane, 1,2-dichloroethane, dichloromethane,

chloroform, methanol, ethanol, and isopropanol, are mentioned, it is not limited to these.

[0044]

2. Photosensitive medium for volume type hologram record
Next, the photosensitive medium for volume type hologram record using the above-mentioned constituent for volume type hologram record is explained.

[0045]

The photosensitive medium for volume type hologram record in this invention provides the photosensitive layer which consists of the above-mentioned constituent on a transparent base material.
The volume hologram characteristic after exposure changes with character of the binder resin which constitutes the constituent.

[0046]

Namely, the case where average molecular weights are 10,000-250,000, and glass transition temperature uses a not less than 80 °C acrylic resin as binder resin, and an average molecular weight by 300,000-1 million. And when glass transition temperature uses vinyl acetate system resin 60 °C or less, the half breadth of a diffraction spectrum is 20 nm or less, and the amount of refractive index modulation of the hologram after volume hologram record is 0.03 or more. On the other hand, when average molecular weights are 10,000-260,000 and glass transition temperature uses vinyl acetate system resin 60 °C or less as binder resin, the half breadth of a diffraction spectrum is not less than 25 nm, and the amount of refractive index modulation is 0.03 or more.

[0047]

The photosensitive medium for volume type hologram record applies on a substrate the coating liquid which consists of the above-mentioned constituent using a spin coater, a photogravure coating machine, a comma coating machine, or a bar coating machine, and it dries and it is obtained by forming a photosensitive layer.

[0048]

As a substrate used for the photosensitive medium for volume type hologram record, What is necessary is just transparency resin etc. which it has, and A polyethylene film, a polypropylene film, A polychloroethylene system film, a polyvinylidene fluoride film, a polyvinylchloride film, A polyvinylidene chloride film, an ethylene-vinyl alcohol film, A polyvinyl alcohol film, a polymethylmethacrylate film, A polyether sulfone film, a polyether ether ketone film, Resin, such as polyester film, such as a polyamide film, a tetrafluoroethylene perfluoroalkyl vinyl ether copolymerization film, and a polyethylene terephthalate film, and a polyimide film, is mentioned.

[0049]

As thickness of this substrate, 2-200 micrometers is 10-50 micrometers preferably. As for especially the coverage of the above-mentioned constituent, it is preferred that 1-100 micrometers of thickness of this coating film after spreading desiccation are set to 10-40 micrometers. When the coating film after desiccation has adhesiveness, this film can be laminated on a spreading side using the film illustrated as the above-mentioned substrate as a protective film. In this case, releasing treatment may be carried out so that it may be easy to remove the contact surface of a laminate film and a spreading side afterwards.

[0050]

3. Record method of volume hologram

In record of a hologram, they are visible laser beams (458 nm), for example, an Ar ion laser. It is recordable on the photosensitive medium for volume type hologram record using laser beams, such as 488 nm, 514.5 nm, krypton ion laser (647.1 nm), helium neon ion laser (633 nm), and an VAG laser (532 nm).

[0051]

As a method of recording a volume type hologram on the photosensitive medium for volume type hologram record, which method of being known from the former may be used.

[0052]

For example, the original edition is stuck in the hologram recording material layer of the photosensitive medium for volume type hologram record, and a volume type hologram is recorded by performing interference exposure using ionizing radiation like visible light or ultraviolet radiation, or an electron beam from the transparent substrate film side.

[0053]

Full exposure, heating, etc. by ultraviolet rays can be suitably processed after interference exposure for promotion of refractive index modulation, and a polymerization reaction conclusion.

[0054]

Thus, in the obtained volume type hologram, a diffraction spectrum can be obtained by measuring a transmissivity spectrum using publicly known art. "Half breadth" [in this invention] The becoming term means the spectral band width in the value of $(T^b - T^p) / 2$ at the time of making transmissivity of T^b and a peak value into T^p for the transmissivity of the baseline of this diffraction spectrum in the wavelength which shows a diffraction peak.

[Work example 1]

[0055]

Example 1

The photosensitive composition solution for volume type hologram record was adjusted using the material shown below.

[0056]

Polymethacrylate
 Polystyrene equivalent-weight average molecular weight: 15,000) 100 weight sections

1, 6-hexanediol diglycidyl ether

(Nagase Chemtex EX-212) 70 weight sections

Diphenoxylethanol fluorene diacrylate

(Osaka Gas BPFEA) 80 weight sections

Diairylodonium salt (product made from low D1A, P12074) 5 weight section

2,5-bis-(4-diethylamino benzylidene) cyclopentanone 1 weight section

1-butanol 30 weight section

Methyl-ethyl-ketone 30 weight section

The bar coating machine was used on a 38-micrometer polyethylene terephthalate (PET) film (Toray Industries lumier T-60), the adjusted above-mentioned solution was applied so that it might become 10 micrometers of dry membrane thickness, and the photosensitive medium for volume type hologram record was produced.

The photosensitive layer side was laminated to the mirror, a 532-nm laser beam was 60-mJ/cm²-entered from the PET side, and the volume type hologram was recorded.

[0057]

Subsequently, the photosensitive layer was fixed by heating and ultraviolet-rays complete exposure, and the volume type hologram was obtained.

About the obtained volume hologram, transmissometry of the spectrophotometer (Shimadzu UVP-C-3100) was performed and calculation of the amount of refractive index modulation (delta n), diffraction efficiency, and half breadth was performed.

[0058]

The diffraction efficiency eta makes transmissivity of T_p and a baseline T_b for the peak transmittance of the obtained transmission spectrum, and is a following formula,

$$\eta = (T_p - T_b) / T_p$$

It is alike, and computes more and half breadth (T_{1/2}) is a following formula about the peak value (T_p) of transmissivity, and one half of the values of the difference of baseline transmissivity (T_p),

$$T_{1/2} = (T_p - T_b) / 2$$

It was alike, and computed more and transmission-spectrum (transmitted wave length) width at the time of T_{1/2} was made into half breadth. delta n was computed with the above-mentioned

Kogelnik theoretical formula using the value of the diffraction efficiency and half breadth which were obtained.

[0059]

Example 2

The photosensitive composition solution for volume type hologram record was adjusted using the material shown below.

Polymethylmethacrylate

(Polystyrene equivalent-weight average molecular weight: 70,000) 100 weight sections

1, 6-hexanediol diglycidyl ether

(Nagase Chemtex EX-212) 70 weight sections

Diphenoxyethanol fluorene diacrylate

(Osaka Gas BPFEA) 80 weight sections

Diaryliodonium salt (product made from low D1A, P12074) 5 weight section

2,5-bis-(4-diethylamino benzylidene) cyclopentanone 1 weight section

1-butanol 30 weight section

Methyl-ethyl-ketone 30 weight section

Like Example 1, volume type hologram production was carried out and measurement about various physical properties was performed.

[0060]

Example 3

The photosensitive composition solution for volume type hologram record was adjusted using the material shown below.

Polymethylmethacrylate

(Polystyrene equivalent-weight average molecular weight: 93,000) 100 weight sections

1, 6-hexanediol diglycidyl ether

(Nagase Chemtex EX-212) 70 weight sections

Diphenoxyethanol fluorene diacrylate

(Osaka Gas BPFEA) 80 weight sections

Diaryliodonium salt (product made from low D1A, P12074) 5 weight section

2,5-bis-(4-diethylamino benzylidene) cyclopentanone 1 weight section

1-butanol 30 weight section

Methyl-ethyl-ketone 30 weight section

Like Example 1, volume type hologram production was carried out and measurement about various physical properties was performed.

[0061]

Example 4

The photosensitive composition solution for volume type hologram record was adjusted using the material shown below.

Polymethylmethacrylate

(Polystyrene equivalent-weight average molecular weight: 120,000) 100 weight sections

1, 6-hexanediol diglycidyl ether
(Nagase Chemtex EX-212) 70 weight sections
Diphenoxylethanol fluorene diacrylate
(Osaka Gas BPFEA) 80 weight sections
Diaryliodonium salt (product made from low DIA, P12074) 5 weight section
2,5-bis-(4-diethylamino benzylidene) cyclopentanone 1 weight section
1-butanol 30 weight section
Methyl-ethyl-ketone 30 weight section
Like Example 1, volume type hologram production was carried out and measurement about various physical properties was performed.
[0062]

Example 5
The photosensitive composition solution for volume type hologram record was adjusted using the material shown below.
Polyvinyl acetate
(Polystyrene equivalent-weight average molecular weight: 500,000) 100 weight sections
1, 6-hexanediol diglycidyl ether
(Nagase Chemtex EX-212) 70 weight sections
Diphenoxylethanol fluorene diacrylate
(Osaka Gas BPFEA) 80 weight sections
Diaryliodonium salt (product made from low DIA, P12074) 5 weight section
2,5-bis-(4-diethylamino benzylidene) cyclopentanone 1 weight section
1-butanol 30 weight section
Methyl-ethyl-ketone 30 weight section
Like Example 1, volume type hologram production was carried out and measurement about various physical properties was performed.
[0063]

Example 6

The photosensitive composition solution for volume type hologram record was adjusted using the material shown below.

Polyvinyl acetate
(Polystyrene equivalent-weight average molecular weight: 83,000) 100 weight sections
1, 6-hexanediol diglycidyl ether
(Nagase Chemtex EX-212) 70 weight sections
Diphenoxylethanol fluorene diacrylate
(Osaka Gas BPFEA) 80 weight sections
Diaryliodonium salt (product made from low DIA, P12074) 5 weight section

2,5-bis-(4-diethylamino benzylidene) cyclopentanone 1 weight section
1-butanol 30 weight section
Methyl-ethyl-ketone 30 weight section
Like Example 1, volume type hologram production was carried out and measurement about various physical properties was performed.

[0064]

Example 7

The photosensitive composition solution for volume type hologram record was adjusted using the material shown below.

Polyvinyl acetate

(Polystyrene equivalent-weight average molecular weight: 100,000) 100 weight sections

1, 6-hexanediol diglycidyl ether

(Nagase Chemtex EX-212) 70 weight sections

Diphenoxylethanol fluorene diacrylate

(Osaka Gas BPFEA) 80 weight sections

Diaryliodonium salt (product made from low DIA, PI2074) 5 weight section

2,5-bis-(4-diethylamino benzylidene) cyclopentanone 1 weight section

1-butanol 30 weight section

Methyl-ethyl-ketone 30 weight section

Like Example 1, volume type hologram production was carried out and measurement about various physical properties was performed.

[0065]

Example 8

The photosensitive composition solution for volume type hologram record was adjusted using the material shown below.

Polyvinyl acetate

(Polystyrene equivalent-weight average molecular weight: 260,000) 100 weight sections

1, 6-hexanediol diglycidyl ether

(Nagase Chemtex EX-212) 70 weight sections

Diphenoxylethanol fluorene diacrylate

(Osaka Gas BPFEA) 80 weight sections

Diaryliodonium salt (product made from low DIA, PI2074) 5 weight section

2,5-bis-(4-diethylamino benzylidene) cyclopentanone 1 weight section

1-butanol 30 weight section

Methyl-ethyl-ketone 30 weight section

Like Example 1, volume type hologram production was carried out and measurement about various physical properties was performed.

[0066]

Example 9

The photosensitive composition solution for volume type hologram record was adjusted using the material shown below.

Polyvinyl acetate

(Polystyrene equivalent-weight average molecular weight: 170,000) 100 weight sections

1, 6-hexanediol diglycidyl ether

(Nagase Chemtex EX-212) 70 weight sections

Diphenoxylethanol fluorene diacrylate

(Osaka Gas BPFEA) 80 weight sections

Dialkylidonium salt (product made from low DIA, P12074) 5 weight section

2,5-bis-(4-diethylamino benzylidene) cyclopentanone 1 weight section

1-butanol 30 weight section

Methyl-ethyl-ketone 30 weight section

Like Example 1, volume type hologram production was carried out and measurement about various physical properties was performed.

[0067]

Example 10

The photosensitive composition solution for volume type hologram record was adjusted using the material shown below.

Polyethylacrylate

(Polystyrene equivalent-weight average molecular weight: 100,000) 100 weight sections

1, 6-hexanediol diglycidyl ether

(Nagase Chemtex EX-212) 70 weight sections

Diphenoxylethanol fluorene diacrylate

(Osaka Gas BPFEA) 80 weight sections

Dialkylidonium salt (product made from low DIA, P12074) 5 weight section

2,5-bis-(4-diethylamino benzylidene) cyclopentanone 1 weight section

1-butanol 30 weight section

Methyl-ethyl-ketone 30 weight section

Like Example 1, volume type hologram production was carried out and measurement about various physical properties was performed.

[0068]

Comparative example 1

The photosensitive composition solution for volume type hologram record was adjusted using the material shown below.

Polyethylmethacrylate

(Polystyrene equivalent-average molecular weight: 120,000) 100 weight sections
 1, 6-hexanediol diglycidyl ether
 (Nagase Chemtex EX-212) 70 weight sections
 Diphenoxylethane fluorine diacrylate
 (Osaka Gas BPEFA) 80 weight sections
 2-mercaptobenzothiazole (made by Aldrich) 5 weight section
 2,5-dinitrobenzyl tosylate 5 weight section
 2,5-bis-(4-diethylamino benzylidene) cyclopentanone 1 weight section
 1-butanol 30 weight section
 Methyl-ethyl-ketone 30 weight section
 Like Example 1, volume type hologram production was carried out and measurement about various physical properties was performed.
 The material physical properties of the used binder resin and the evaluation result of a volume hologram are shown in Table 1.

[Table 1]

表 1 バイナリー樹脂の材料物性および体積ホログラムの評価結果

樹脂	Tg (°C)	分子重*	Δn	回折効率 (%)	半価幅 (mm)	バイナリー樹脂	
						評価	詳細
実施例 1	98	15,000	0.031	60	20	ポリメチルメタクリレート	実施例 1
実施例 2	105	70,000	0.035	90	18	ポリメチルメタクリレート	実施例 2
実施例 3	110	93,000	0.034	93	17	ポリメチルメタクリレート	実施例 3
実施例 4	114	120,000	0.031	95	15	ポリメチルメタクリレート	実施例 4
実施例 5	45	500,000	0.032	80	18	ポリ酢酸ビニル	実施例 5
実施例 6	43	83,000	0.050	70	30	ポリ酢酸ビニル	実施例 6
実施例 7	45	100,000	0.047	80	28	ポリ酢酸ビニル	実施例 7
実施例 8	30	260,000	0.044	76	25	ポリ酢酸ビニル	実施例 8
実施例 9	45	170,000	0.050	84	27	ポリ酢酸ビニル	実施例 9
実施例 10	—24	100,000	0.065	74	38	ポリエチルメタクリレート	実施例 10
比較例 1	122	300,000	0.029	98	13.6	ポリメチルメタクリレート	比較例 1

* ポリメチルメタクリレート

[Translation done.]

PATENT ABSTRACTS OF JAPAN

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KANO YOSHINORI

(54) PHOTSENSITIVE MATERIAL FOR HOLOGRAM, RECORDING MEDIUM FOR HOLOGRAM AND PRODUCTION OF HOLOGRAM USING THE SAME

(57)Abstract:

PURPOSE: To provide a photosensitive material for a hologram having excellent chemical stability, environmental resistance, high sensitivity, high refraction efficiency and high resolution, and to provide a recording medium for a hologram and a producing method of a hologram using this material.

CONSTITUTION: This photosensitive material for a hologram consists of a high mol.wt. polymer having fluorine atoms, a compd. having polymerizable functional groups, and a photopolymer, initiator which is activated by exposure to radiation having a chemical effect, and a solvent which does not dissolve the high mol.wt. polymer containing fluorine atoms but dissolves the compd. having polymerizable functional groups. The high mol.wt. polymer material having fluorine atoms is dispersed in a granular state in a soln. This photosensitive material for a hologram is applied on a base body to obtain a hologram recording medium. The obtd. recording medium is exposed by interference of laser beam and exposed to active rays or heated to obtain a hologram having ≥ 0.005 refractive index modulation degree.

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(54) 発明の名称) ホログラム用感光材料、ホログラム用記録媒体およびそれを用いたホログラムの製造方法

(57) 【要約】

【目的】化学的安定性及び耐環境性に優れ、高感度、高回折効率および高解像度な特性を有するホログラム用感光材料およびホログラム用記録媒体ならびにそれを用いたホログラムの製造方法を提供することを目的とする。
【構成】7ツ素原子を有する高分子重合体、重合可能な官能基を有する化合物、および化学作用媒の露光により活性化する光重合開始剤系、および7ツ素原子を有する高分子重合体を溶解しないような重合可能な官能基を有する化合物を溶解する溶剤からなり、7ツ素原子を有する高分子重合体が溶液中に粒子状に分散したホログラム用感光材料であって、該ホログラム用感光材料を基板上に塗布して形成されたホログラム用記録媒体にレーザー光による干渉露光した後、活性化膜による露光または加熱を施すことで0.005以上の回折率を測定するホログラムを製造する。

【請求項1】 フッ素原子を含有する高分子重合体

料、半ロウア登録標本と、それを引用した半ロウアの

* 972 (099) 684-727 (可接)

[Z000]

【健康の技術】米ロシラ公は三次元画像の記録、再生

か可能なことから、その限りでは、裁量性効果を得

カエリ、香琳、維新寺の表紙、FOP(なぞり)入り

1. キノコは、キノコ科に属する。また、キノコは、キノコ目、キノコ綱、キノコ門、キノコ界、キノコ界に属する。

環境は、人々の生活に与える影響が大きい。環境を改善することは、人々の生活の質を向上させることに役立つ。

小田のフーカなどは、活用されている。特に外資は田畑

2. 孝順の奉養西ノ川中村調書に? 年々口年 村? 年々口年
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本報社址：上海南京路

ロゾワ人を通過する米を監視することが可能となるが

め、ポイントカード用途の他に、POS用スキーマーお上

び入ったグラフィクス (HUD) に代表されるホ

ロケラ公光字素子 (HOE) の応用が期待されている

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【0003】このような産業上における体積位相型ホロ

グラフへの要望から、フォトボリマーを利用した体積位

相型ホログラム記録材料の提案がこれまでにあってい

る。例えば、フオトリターを用いたホログラムの製造

方差として、7オトボリ2一からなるホログラム記録

体を輻射線の干渉パターンに露光した後、現像液による

環境問題を解決する方法が提案されていゝ。例えは特公開6

2-22152号においては、相体となるべき重合体

に、2圖以上の主として女性小童和服を有する多目的車

星村および元重吉の組別とを組み合わせる、編別

第1の工程、該部材を第1

威德、野丁、乙南、乙中、乙北、乙西、乙東、乙南、乙中、乙北、乙西、乙東、乙南、乙中、乙北、乙西、乙東

市井の生活、第2の組用で死に臨む山村を収束させる。

[illegible][illegible]

● 2006年10月1日現在、141万4千171戸が、1000万円以上の資産を保有している。これは、2005年10月1日現在と比べて、約10万戸増加している。

上表の2、4、5、6、7、8、9、10、11、12、13、14、15、16、17、18、19、20、21、22、23、24、25、26、27、28、29、30、31、32、33、34、35、36、37、38、39、40、41、42、43、44、45、46、47、48、49、50、51、52、53、54、55、56、57、58、59、60、61、62、63、64、65、66、67、68、69、70、71、72、73、74、75、76、77、78、79、80、81、82、83、84、85、86、87、88、89、90、91、92、93、94、95、96、97、98、99、100、101、102、103、104、105、106、107、108、109、110、111、112、113、114、115、116、117、118、119、120、121、122、123、124、125、126、127、128、129、130、131、132、133、134、135、136、137、138、139、140、141、142、143、144、145、146、147、148、149、150、151、152、153、154、155、156、157、158、159、160、161、162、163、164、165、166、167、168、169、170、171、172、173、174、175、176、177、178、179、180、181、182、183、184、185、186、187、188、189、190、191、192、193、194、195、196、197、198、199、200、201、202、203、204、205、206、207、208、209、210、211、212、213、214、215、216、217、218、219、220、221、222、223、224、225、226、227、228、229、230、231、232、233、234、235、236、237、238、239、240、241、242、243、244、245、246、247、248、249、250、251、252、253、254、255、256、257、258、259、260、261、262、263、264、265、266、267、268、269、270、271、272、273、274、275、276、277、278、279、280、281、282、283、284、285、286、287、288、289、290、291、292、293、294、295、296、297、298、299、300、301、302、303、304、305、306、307、308、309、310、311、312、313、314、315、316、317、318、319、320、321、322、323、324、325、326、327、328、329、330、331、332、333、334、335、336、337、338、339、340、341、342、343、344、345、346、347、348、349、350、351、352、353、354、355、356、357、358、359、360、361、362、363、364、365、366、367、368、369、370、371、372、373、374、375、376、377、378、379、380、381、382、383、384、385、386、387、388、389、390、391、392、393、394、395、396、397、398、399、400、401、402、403、404、405、406、407、408、409、410、411、412、413、414、415、416、417、418、419、420、421、422、423、424、425、426、427、428、429、430、431、432、433、434、435、436、437、438、439、440、441、442、443、444、445、446、447、448、449、450、451、452、453、454、455、456、457、458、459、460、461、462、463、464、465、466、467、468、469、470、471、472、473、474、475、476、477、478、479、480、481、482、483、484、485、486、487、488、489、490、491、492、493、494、495、496、497、498、499、500、501、502、503、504、505、506、507、508、509、510、511、512、513、514、515、516、517、518、519、520、521、522、523、524、525、526、527、528、529、530、531、532、533、534、535、536、537、538、539、540、541、542、543、544、545、546、547、548、549、550、551、552、553、554、555、556、557、558、559、560、561、562、563、564、565、566、567、568、569、570、571、572、573、574、575、576、577、578、579、580、581、582、583、584、585、586、587、588、589、590、591、592、593、594、595、596、597、598、599、600、601、602、603、604、605、606、607、608、609、610、611、612、613、614、615、616、617、618、619、620、621、622、623、624、625、626、627、628、629、630、631、632、633、634、635、636、637、638、639、640、641、642、643、644、645、646、647、648、649、650、651、652、653、654、655、656、657、658、659、660、661、662、663、664、665、666、667、668、669、670、671、672、673、674、675、676、677、678、679、680、681、682、683、684、685、686、687、688、689、690、691、692、693、694、695、696、697、698、699、700、701、702、703、704、705、706、707、708、709、710、711、712、713、714、715、716、717、718、719、720、721、722、723、724、725、726、727、728、729、730、731、732、733、734、735、736、737、738、739、740、741、742、743、744、745、746、747、748、749、750、751、752、753、754、755、756、757、758、759、760、761、762、763、764、765、766、767、768、769、770、771、772、773、774、775、776、777、778、779、780、781、782、783、784、785、786、787、788、789、790、791、792、793、794、795、796、797、798、799、800、801、802、803、804、805、806、807、808、809、810、811、812、813、814、815、816、817、818、819、820、821、822、823、824、825、826、827、828、829、830、831、832、833、834、835、836、837、838、839、840、841、842、843、844、845、846、847、848、849、850、851、852、853、854、855、856、857、858、859、860、861、862、863、864、865、866、867、868、869、870、871、872、873、874、875、876、877、878、879、880、881、882、883、884、885、886、887、888、889、890、891、892、893、894、895、896、897、898、899、900、901、902、903、904、905、906、907、908、909、910、911、912、913、914、915、916、917、918、919、920、921、922、923、924、925、926、927、928、929、930、931、932、933、934、935、936、937、938、939、940、941、942、943、944、945、946、947、948、949、950、951、952、953、954、955、956、957、958、959、960、961、962、963、964、965、966、967、968、969、970、971、972、973、974、975、976、977、978、979、980、981、982、983、984、985、986、987、988、989、990、991、992、993、994、995、996、997、998、999、1000、1001、1002、1003、1004、1005、1006、1007、1008、1009、1010、1011、1012、1013、1014、1015、1016、1017、1018、1019、1020、1021、1022、1023、1024、1025、1026、1027、1028、1029、1030、1031、1032、1033、1034、1035、1036、1037、1038、1039、1040、10

2. ある1台車ロケの撮影に於いて、撮影準備段階を

許敬餘評張 女中 許敬餘の『張敬餘の女中』について

作中に生じる空間や人物の配置に起因する想像力や内化

による降雨時の低下率の調査結果が示すところから、

2927

【0004】一方、ホログラムの製造工程において、

なあるいは相違な湿式処理工程を必要としない、唯一の

処理工程として干渉露光のみでホログラムを製造すること

とが可能なフットポリマーを使ったホログラム記録材料

およびその製造法が開示されている。例えば、米国特許

3, 658, 526においては、脂肪族系高分子バイソ

ターと脂肪族系アクリルモノマーおよび光重合開始剤が

らなることを特徴とするホログラム記録用感光性層が提

[illegible]

[illegible]

(a) (X₉) フリル酸エチレン類; (X₈) フリル酸メチル、(X₇) フリル酸エチル、(X₆) フリル酸プロピル、(X₅) フリル酸ブチル、(X₄) フリル酸ペンチル、(X₃) フリル酸ヘキシル、(X₂) フリル酸セptyル、(X₁) フリル酸オクチルなどの(X₉) フリル酸のC_nないしC₁₈の

[illegible]

与わせたものが好適に使用される。さらに、トリクロロ
 トリフルオロエタン、メタキシレンヘキサフルオライ
 ド、テトラクロロヘキサフルオロタンなども必要によ

エチル、酢酸エチル、酢酸メチル、酢酸プロピル、2-エチルヘキシルアセートが挙げられ、これらはそれぞれ単独で用いても、2種以上で混合して用いることもできるが、一般には脂肪酸エステル水素を主体とし、これに適宜芳香族化水素や上記の如きアルキル系、エチル系、エステル系またはケトン系溶剤を組み

[illegible]

て、對子状に生成した重合体の分配性を決定する。銅能

【015】本発明で使用される、溶液中に粒子状に分
散されたアクリル系含有高分子重合体は、前記
した方法で製造したアクリル系含有高分子を分散剤と
して、本発明の分散剤として用いられる。

ある。これらは単独あるいは2種以上を種々の割合で混合して使用することもできる。反応温度、反応圧力は、重

2

おち空周波数(周波度)が高くなるのは、感光板に對しこれらの光束も平行に入射された時、すなわち $\theta_0 = 18.0^\circ$ 、 $\theta_R = 0^\circ$ の条件の時である。この場合、 D は式(A)によって算出される。

0.6 m以下であり、より好ましくは平均粒子径は、0.2 m以下である。その理由として、本発明における粒子状の高分子重合体を使用して体積位相型のホログラムを製造するに当たり、第1回図に示したような平均粒子径に2.5 m未満の距離を隔てて配置する場合には、第1回図に示したような粒子が形成される。

【0019】また、本発明で使用されるフッ素原子を含むフッ素含有する高分子重合体の濃度は、一般的に30から70重量%の範囲が好ましい。

【0018】この様な、溶液中に粒子状に分散されたアクリル酸含有高分子重合体を製造するに当てては、前記の分散安定剤としての機能を持つアクリル酸含有高分子重合体の使用量を、得られる高分子重合体の膨張率に対して3~70重量%の範囲で使用することが好都合である。さらに、有機液体中に粒子状に分散されたアクリル酸含有高分子重合体の使用量を、得られる高分子重合体の膨張率に対して3~70重量%の範囲で使用することが好都合である。

[illegible][illegible]

(X₃) フリール、E フロキシロル (X₃)
 フリールなどの (X₃) フリール酸のC₁₈
 のE フロキシロル、フリールエチル
 (X₃) フリールなどの (X₃) フリール酸のC₃
 ないC₁₈のアルキルエチルなど、

フルキエス、フリシル(×) フクリート、
フリン(×) フクリートなどの(×) フクリン酸
のC2ないC8のアルケニルエス、ヒドロキシエチ

特開平8-272284

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05

64-17048号記載のチン素類、特開平2-291

560号記載のO-アブチオキとプロキオキとN-

アルキオキシジシブチン素類なども挙げられる。連続移

動剤の使用量は、フッ素原子を含有する高分子重合体

の100重量部に対して1.0〜30重量部が好ま

しい。

【0040】本発明のホログラム用感光材料は、溶剤中

に粒子状分散したフッ素原子を含有する高分子重合体

(A)の分散液に、光重合開始剤(C)（増感剤

）と溶剤(II)（I）及び重合可能な官能基を1つに

上付する化合物(B)）さらには連続移動剤を1つに

配合させて使用される。上記各成分の配合比はに特定の

範囲に在り、照射に供する光源から放射される光の波

長が1μ以上となるように増感剤の濃度を調整するこ

とが好ましい。また、本発明のホログラム用感光材料に

は、照射による光重合を防止する目的で重合禁止剤を加

することが可能である。具体例としては、P-メチルシ

ブチルニトロソアミンまたはクロアチルニトロソアミン

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【0044】得られた感光液は、基板上に液状に塗布

し、1〜15重量部の範囲で使用される。

(A) 100重量部に対し、0.1〜20重量部、好ま

しくは1〜5重量部の範囲で使用される。

【0048】

光、さらには電子線をを用いることも可能である。

【0047】また、全面露光に使用する光源としては、

【0047】また、全面露光に使用する光源としては、

【0047】また、全面露光に使用する光源としては、

【0047】また、全面露光に使用する光源としては、

【作用】本発明のホログラム用感光材料は、フッ素原子

を含有する高分子重合体(A)、重合可能な官能基を有

する化合物(B)、光重合開始剤系(C)をおよび溶解

(D)から成る組成物において、フッ素原子を含有する

高分子重合体(A)が溶液中に粒子状に分散してなるこ

と特徴とする。感光材料を基板上に露として形成し

て得られるホログラム用記録媒体を供て、第1図に示

したようなコシエント性の高い一方向の干渉照

光に照射しては、前記した式(A)に従った干渉パター

ンが記録媒体中に形成される。その時、干渉作用の強い

部位においては、光的作用によって、該光重合開始剤系

から生じた重合体(A)の重合反応が促進される。一方、

干渉作用の低い部位では、このような重合反応は顕著に

生ず。同様に、重合反応に伴う体積収縮によって生

じる屈折率差が形成される。また、干渉作用の強い部

位には、反応の重合可能な化合物(B)が収縮によって

集まるため、さらに濃度が上がり、干渉作用の強い部

位との屈折率差が拡大することになり、屈折率差によ

るホログラムが形成される。特に本発明においては、粒

子状の高分子重合体(A)を使用することと特徴としてお

り、粒子状の高分子重合体から形成される皮膜であるが

ために、通常の溶解性のある高分子(ポリアクリレートと

重合可能な官能基を有する化合物(B)の皮膜中における

収縮が顕著となり、屈折率差が顕著になったものと推察

される。その理由は明らかではないが、粒子同士の接着に

よって形成される皮膜の比較的小さいストロークが、重合

可能な官能基を有する化合物(B)の重合収縮の方向の

経路となったものと推察される。

【0049】一方、本発明において使用される、高分子

重合体(A)と、重合可能な官能基を有する化合物

とを組合せ、さらに屈折率差を顕著に選択すること

によって、さらに屈折率差増強を向上させること

が可能となり、0.005以上の屈折率差を示す組

合の時、その効果は顕著になったものと解釈され

る。また、このような組合せは、高分子重合体(A)

と重合可能な官能基を有する化合物(B)との組合せ

においてだけでなく、屈折率の互いに異なる2種類以上

の、重合可能な官能基を有する化合物(B)を組み合わ

せた時にも実現可能で、その場合、使用した重合可能な

官能基を有する化合物(B)が、互いに反応性に差があ

【0051】製造例1

【実施例】以下実施例に基づき、本発明をより詳細に説

明する。以下の各例において、部は特に断りのない限り

重量部を表す。

フッ素原子を含有する高分子重合体の粒子状分散液(A)の製造

例1

フッ素原子を含有する高分子重合体の粒子状分散液(A)の製造

例1

フッ素原子を含有する高分子重合体の粒子状分散液(A)の製造

例1

フッ素原子を含有する高分子重合体の粒子状分散液(A)の製造

例1

フッ素原子を含有する高分子重合体の粒子状分散液(A)の製造

例1

フッ素原子を含有する高分子重合体の粒子状分散液(A)の製造

例1

フッ素原子を含有する高分子重合体の粒子状分散液(A)の製造

例1

フッ素原子を含有する高分子重合体の粒子状分散液(A)の製造

例1

*クロヘキシノールシリレート (DCPA、日立化成アクリルモノリファ-A-513) と、25部のエチルソキサイドを混合してアセトニールシリレート (B) P-4B、共結晶阻凝剤) に変えた他は、実施例1と同様の方法で操作した時の結果を、表2にまとめて示した。

【0061】実施例6

実施例1における50部のDCPDを、25部のDCPDと25部のフェノキシエチルシリレート (POE-A、大阪有機化学工業製：ビスコート#192) に変えた他は、実施例1と同様の方法で操作した時の結果を、表2にまとめて示した。

【0062】実施例7

実施例1における50部のDCPDを、25部のDCPDと25部のエチルシリレート (PDAと25部のDCPDを、25部のDCPDと25部のフェノキシエチルシリレート (POESA) に変えた他は、実施例1と同様の方法で操作した時の結果を、表2にまとめて示した。

【0063】実施例8

実施例1における50部のDCPDを、25部のDCPDと25部のフェノキシエチルシリレート (POESA) に変えた他は、実施例1と同様の方法で操作した時の結果を、表2にまとめて示した。

【0064】実施例9

実施例1における50部のDCPDを、全てPOESAに変えた他は、実施例1と同様の方法で操作した時の結果を、表2にまとめて示した。

【0065】

【表1】

実施例1における50部のDCPDを、25部のシリ*30

| 重合可能な
官能基を有
する化合物
(重量部) | 増粘剤
(重量部) | 開始剤
(重量部) |
|----------------------------------|--------------|--------------|
|----------------------------------|--------------|--------------|

| | | | |
|---|-----------------------|----------|-------|
| 1 | DCPD(50) | KCD(0.5) | DP(2) |
| 2 | DCPD(50) | KCD(0.5) | DP(2) |
| 3 | DCPD(25)+BGA(25) | KCD(0.5) | DP(2) |
| 4 | DCPD(25)+BGA(25) | KCD(0.5) | DP(2) |
| 5 | PAS13A(25)+BP-4EA(25) | KCD(0.5) | DP(2) |
| 6 | DCPD(25)+POEA(25) | KCD(0.5) | DP(2) |
| 7 | DCPD(25)+SBOA(25) | KCD(0.5) | DP(2) |
| 8 | DCPD(25)+POESA(25) | KCD(0.5) | DP(2) |
| 9 | POEA(50) | KCD(0.5) | DP(2) |

*フェノキシエチルシリレートを含む成分分子重合体は、製造例1にて得られた化合物(48重量部)を使用した。

※【表2】

【0066】

た。正反射波以外で最も大きな値と、試料を置かず直接入射光を受光したときの値との比を回折効率とした。表2に、得られたホログラム特性の結果をまとめて示した。尚、屈折率変調度 (Δn) は式(5)を用いて算出した。

$$\Delta n = \lambda \cdot \tan h^{-1} (n^2)^{-1} \cdot \cos \theta$$

$\pi \cdot d$

(ここで、 λ は照射波長、 n は回折効率、 d は厚さ、 θ は45°を表す。)

【0057】実施例2

実施例1における50部のDCPDを、全てシマクロ

ールトリクロロペンチアクリレート (DCCPS

A) に変えた他は、実施例1と同様の方法で操作した時

の結果を、表2にまとめて示した。

【0058】実施例3

実施例1における50部のDCPDを、25部のDC

PDと、25部のオキシベンチルトリクロロシリ

ート (NP-GA、新中村化学社製) に変えた他は、実

施例1と同様の方法で操作した時の結果を、表2にまと

めて示した。

【0059】実施例4

実施例1における50部のDCPDを、25部のDC

PDと、25部の2-(2-クロキシー-1,1-

ジメチル)-5-エチル-5'-ヒドロキシマ

ル-1,3-ジエキサンジフルリレート (R-604、

日本化薬社製) に変えた他は、実施例1と同様の方法で

操作した時の結果を、表2にまとめて示した。

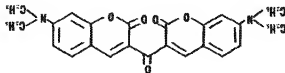
【0060】実施例5

実施例1における50部のDCPDを、25部のシリ*30

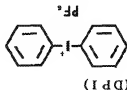
実施例 10 溶液濃度 0.01% (g/ml) 照射強度 100mW/cm² 照射時間 10分

| 実施例 | 溶液濃度 (g/ml) | 照射強度 (mW/cm ²) | 照射時間 (分) | 照射効率 (%) | 照射効率 (100倍) | 照射効率 (1000倍) |
|-----|-------------|----------------------------|----------|----------|-------------|--------------|
| 1 | 4.88 | 2.0 | 15 | 7.0 | 0.89 | 4.87 |
| 2 | 4.88 | 3.0 | 15 | 7.2 | 0.92 | 4.87 |
| 3 | 4.88 | 3.0 | 15 | 6.9 | 0.79 | 4.88 |
| 4 | 4.88 | 2.0 | 15 | 7.0 | 0.89 | 4.88 |
| 5 | 4.88 | 2.5 | 15 | 8.2 | 1.10 | 4.87 |
| 6 | 4.88 | 2.5 | 15 | 8.7 | 1.23 | 4.87 |
| 7 | 4.88 | 3.0 | 15 | 7.5 | 0.96 | 4.90 |
| 8 | 4.88 | 2.5 | 15 | 7.0 | 0.89 | 4.89 |
| 9 | 4.88 | 3.5 | 15 | 7.7 | 1.00 | 4.90 |

* 10 * 【化1】



(KCD)



(DP1)

【0068】実施例10～18 ※に操作した時の結果を、表4にまとめて示した。

【0069】

【表3】

実施例1～9における各感光液に、連鎖移動剤として2-メルカプトベンズエキサン-5-オール (MBO) 5部さらに加えて調整した感光液を用いた例は、実施例1～9同様※

重合可能な官能基を有する化合物 (重合部)
連鎖移動剤 (重合部)
開始剤 (重合部)

| | | | | |
|----|---------------------|---------|-----------|---------|
| 10 | PCPA (50) | MBO (5) | KCD (0.5) | DP1 (2) |
| 11 | PCPA (50) | MBO (5) | KCD (0.5) | DP1 (2) |
| 12 | PCPA (25)+MBO (25) | MBO (5) | KCD (0.5) | DP1 (2) |
| 13 | PCPA (25)+MBO (25) | MBO (5) | KCD (0.5) | DP1 (2) |
| 14 | PCPA (25)+MBO (25) | MBO (5) | KCD (0.5) | DP1 (2) |
| 15 | PCPA (25)+PCSA (25) | MBO (5) | KCD (0.5) | DP1 (2) |
| 16 | PCPA (25)+PCSA (25) | MBO (5) | KCD (0.5) | DP1 (2) |
| 17 | PCPA (25)+PCSA (25) | MBO (5) | KCD (0.5) | DP1 (2) |
| 18 | PCPA (50) | MBO (5) | KCD (0.5) | DP1 (2) |

* フッ素原子を含有する高分子重合体は、製造例1にて得られた化合物 (48重量部) を使用した。

* * 【表4】

【0070】

32

| 項目 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 | 32 | 33 | 34 | 35 | 36 | 37 | 38 | 39 | 40 | 41 | 42 | 43 | 44 | 45 | 46 | 47 | 48 | 49 | 50 | 51 | 52 | 53 | 54 | 55 | 56 | 57 | 58 | 59 | 60 | 61 | 62 | 63 | 64 | 65 | 66 | 67 | 68 | 69 | 70 | 71 | 72 | 73 | 74 | 75 | 76 | 77 | 78 | 79 | 80 | 81 | 82 | 83 | 84 | 85 | 86 | 87 | 88 | 89 | 90 | 91 | 92 | 93 | 94 | 95 | 96 | 97 | 98 | 99 | 100 |
|----|---|---|---|---|---|---|---|---|---|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|-----|
| 項目 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 | 32 | 33 | 34 | 35 | 36 | 37 | 38 | 39 | 40 | 41 | 42 | 43 | 44 | 45 | 46 | 47 | 48 | 49 | 50 | 51 | 52 | 53 | 54 | 55 | 56 | 57 | 58 | 59 | 60 | 61 | 62 | 63 | 64 | 65 | 66 | 67 | 68 | 69 | 70 | 71 | 72 | 73 | 74 | 75 | 76 | 77 | 78 | 79 | 80 | 81 | 82 | 83 | 84 | 85 | 86 | 87 | 88 | 89 | 90 | 91 | 92 | 93 | 94 | 95 | 96 | 97 | 98 | 99 | 100 |

10*【0073】美標例21

[illegible]

た。また、実験例1と同様の方法で操作した時の結果を、
【0074】実験例22

実施例1における50部のDCPDAと、25部のDC
PAと25部のビスフェノールAノリシマル
（エポト807、油化シェルビス社製）に変え
た。実施例1と同様の方法で操作した時の結果を、表6に示し
【表5】

美6に於て示した。

| 天海例 | 直付可能
任意金支
付に付合
物 | 諸般付合
物(重要部) | 共同付合
物(重要部) | 附合付
物(重要部) |
|-----|---------------------------|----------------|----------------|---------------|
| 1 9 | BP-4E4(25)+E14,4221(25) | なし | KCD(0.5) | DP1(2) |
| 2 0 | DCP4(25)+P807(25) | なし | KCD(0.5) | DP1(2) |
| 2 1 | DCP4(25)+PCE-B(25) | なし | KCD(0.5) | DP1(2) |
| 2 2 | POE4(25) | なし | KCD(0.5) | DP1(2) |

*フッ素原子を含有する高分子重合体は、製造例1にて得られた化合物(48重量部)を使用した。

【9望】※ ※

| 实验号 | 面积比 | 质量比 | 摩尔比 | 百分组成 | 分子量 |
|-----|------|-----|-----|------|------|
| 1 | 4.88 | 3.0 | 1.5 | 8.1 | 1.23 |
| 2 | 4.88 | 3.5 | 1.5 | 6.0 | 0.76 |
| 3 | 4.88 | 1.5 | 1.5 | 6.8 | 0.86 |
| 4 | 4.88 | 1.5 | 1.5 | 7.7 | 1.00 |
| 5 | 4.88 | 4.0 | 1.5 | 4.0 | 1.00 |

★ 47.

[illegible]

| | |
|---|-----------------------------|
| 実験例10における0.5部のナ
オキヤンテッド実験体(TXD)に変えた例は、実験例1 | 0と同様の方法で操作した時の結果を表8に示して示*50 |
| 実験例10における0.5部のナ
オキヤンテッド実験体(TXD)に変えた例は、実験例1 | 0と同様の方法で操作した時の結果を表8に示して示*50 |

* 実施例10と同様の方法で操作した時の結果を表8にま

とめて示した。

【0083】実施例29

実施例10における0.5部のKCDを、0.5部のチ

トリス(2,2,2-トリフルオロエタノール)誘導体(TPZD)に変

え、光源にHe-Neレーザの633nm光を使用し

た。実施例10と同様の方法で操作した時の結果を

表8にまとめて示した。

【0084】

【表7】

にHe-Neレーザの633nm光を使用した。*

| 実施例 | 重合可能な
可溶性化合物
(重量部) | 連鎖移動剤
(重量部) | 増感剤
(重量部) | 開始剤
(重量部) |
|-----|--------------------------|----------------|--------------|--------------|
|-----|--------------------------|----------------|--------------|--------------|

| | | | | |
|----|----------|-------|-----------|-------|
| 23 | DCPD(50) | MB(5) | Ba結晶(1.0) | DP(2) |
| 24 | DCPD(50) | MB(5) | TD(0.5) | DP(2) |
| 25 | DCPD(50) | MB(5) | MD(0.3) | DP(2) |
| 26 | DCPD(50) | MB(5) | DEA(0.5) | DP(2) |
| 27 | DCPD(50) | MB(5) | PD(0.2) | DP(2) |
| 28 | DCPD(50) | MB(5) | TPZD(0.2) | DP(2) |
| 29 | DCPD(50) | MB(5) | TPZD(0.5) | DP(2) |

*7-オキソノルボルネン系含有する高分子重合体は、製造例1にて得られた化合物
(48重量部)を使用した。

【0085】

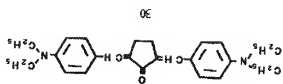
| 実施例 | 重合可能な
可溶性化合物
(重量部) | 連鎖移動剤
(重量部) | 増感剤
(重量部) | 開始剤
(重量部) |
|-----|--------------------------|----------------|--------------|--------------|
|-----|--------------------------|----------------|--------------|--------------|

| | | | | | | |
|----|------|----|----|----|------|-----|
| 23 | 4.41 | 30 | 16 | 67 | 0.72 | 440 |
| 24 | 4.88 | 45 | 16 | 70 | 0.83 | 487 |
| 25 | 4.88 | 50 | 16 | 86 | 0.78 | 487 |
| 26 | 4.88 | 85 | 16 | 72 | 0.86 | 487 |
| 27 | 6.76 | 80 | 16 | 77 | 1.30 | 676 |
| 28 | 6.38 | 10 | 16 | 75 | 1.17 | 638 |
| 29 | 6.38 | 35 | 16 | 72 | 1.11 | 638 |

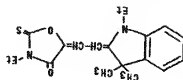
【0086】

* 【化2】

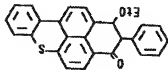
【0087】
【化3】



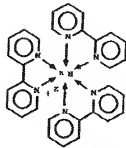
(DEAW)



(MCD)



(TXD)



(Ru配合体)

35 (19)

特開平8-272284

て示した。

【0089】実施例31

実施例10における2部のDPIを、2部の2,4,6

トリリス（トリクロメル）-1,3,5-トリアジ

ン（TCT）に変えた他は、実施例10と同様の操作を

した時の結果を表10にまとめて示した。

【0090】実施例32

実施例10における2部のDPIを、2部のN-アセ

ルリレン（NPG）に変えた他は、実施例10と同様

の操作をした時の結果を表10にまとめて示した。

【0091】実施例33

実施例10における2部のDPIを、2部のベンブレン

錯体（4-ルンギエア-261；IRG261）に変えた

他は、実施例10と同様の操作をした時の結果を表10

にまとめて示した。

【0092】実施例34

実施例10における2部のDPIを、2部のジメチル

エチルサルホニウムトリフェニルホルボレート（DM

PSB）に変えた他は、実施例10と同様の操作をした

時の結果を表10にまとめて示した。

【0093】実施例35

実施例10における2部のDPIを、2部のチトラチ

ルフェニウムトリフェニルホルボレート（TBA

B）に変えた他は、実施例10と同様の操作をした時の

結果を表10にまとめて示した。

【0094】実施例36

実施例10における2部のDPIを、2部のジフェニル

アミルサルホニウムトリフェニルホルボレート

（DPSB）に変えた他は、実施例10と同様の操作

をした時の結果を表10にまとめて示した。

【0095】実施例37

実施例10における2部のDPIを、2部のベンブレン

トリフェニルホルボレート（FEB）に変えた他

は、実施例10と同様の操作をした時の結果を表10に

まとめて示した。

【0096】実施例38

実施例10における2部のDPIを、2部のジフェニル

ヨードニウムトリフェニルホルボレート（DPIB）

に変えた他は、実施例10と同様の操作をした時の結果

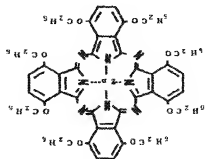
を表10にまとめて示した。

【0097】

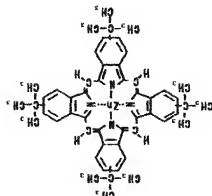
【表9】

実施例10における2部のDPIを、2部の3,3',4,4'-チトラキス（トリフェニルホルボレート）（BTPB）に変えた他は、実施例10と同様の操作をした時の結果を表10にまとめ

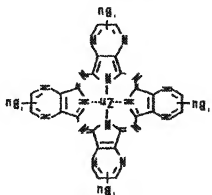
(PCD)



(TBPB)



(TPZD)



重合可能な
官能基を有
する化合物
(重量部)
増粘剤
(重量部)
閉結剤
(重量部)

| | | | |
|-----------|--------|----------|----------|
| DCPDA(50) | MEK(5) | KCD(0.5) | BITB(2) |
| DCPDA(50) | MEK(5) | KCD(0.5) | TCT(2) |
| DCPDA(50) | MEK(5) | KCD(0.5) | NFC(2) |
| DCPDA(50) | MEK(5) | KCD(0.5) | IR261(2) |
| DCPDA(50) | MEK(5) | KCD(0.5) | DMP5B(2) |
| DCPDA(50) | MEK(5) | KCD(0.5) | TBAB(2) |
| DCPDA(50) | MEK(5) | KCD(0.5) | DPP5B(2) |
| DCPDA(50) | MEK(5) | KCD(0.5) | FAB(2) |
| DCPDA(50) | MEK(5) | KCD(0.5) | DP18(2) |

* アラキル基を含有する高分子重合体は、製造例1にて得られた化合物
(48重量部)を使用した。

* [表10]

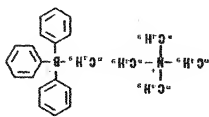
| 製造例 | 厚さ
(mm) | 屈折率
(n_D^{20}) | 密度
(g/cm^3) | 吸光度
(%) | 厚さ
(mm) | 屈折率
(n_D^{20}) | 密度
(g/cm^3) | 吸光度
(%) |
|-----|------------|-----------------------|--------------------|------------|------------|-----------------------|--------------------|------------|
| 30 | 4.88 | 80 | 1.6 | 7.3 | 0.87 | 4.87 | | |
| 31 | 4.88 | 80 | 1.6 | 7.3 | 0.87 | 4.87 | | |
| 32 | 4.88 | 50 | 1.6 | 7.0 | 0.83 | 4.87 | | |
| 33 | 4.88 | 30 | 1.6 | 7.2 | 0.86 | 4.87 | | |
| 34 | 4.88 | 25 | 1.6 | 7.5 | 0.90 | 4.87 | | |
| 35 | 4.88 | 35 | 1.6 | 7.3 | 0.87 | 4.87 | | |
| 36 | 4.88 | 25 | 1.6 | 7.2 | 0.80 | 4.87 | | |
| 37 | 4.88 | 25 | 1.6 | 7.5 | 0.87 | 4.87 | | |
| 38 | 4.88 | 15 | 1.6 | 7.3 | 0.87 | 4.87 | | |

[0098]

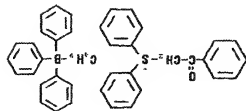
[0099]
[化4]

42

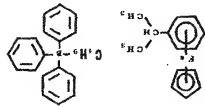
(TBA B)



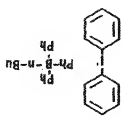
(D P S B)



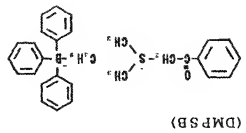
(F e A B)



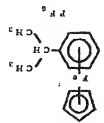
(D P I B)



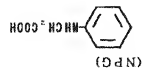
30



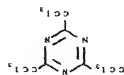
(DMF S B)



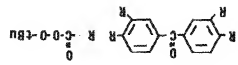
(I R G 2 6 I)



(N P G)



(T C T)



(B T T B)

41

【化5】
【1000】

【10101】実施例39
実施例34における0.5部のKCDを0.3部の7-
ニフテニル誘導体(C7D)に変えた他は、実施例34と同様
の操作をした時の結果を表12にまとめて示した。

【10102】実施例40

実施例34における0.5部のKCDを0.3部のスチ
リル誘導体(S7D)に変えた他は、実施例34と同
様の操作をした時の結果を表12にまとめて示した。

【10103】実施例41

実施例34における0.5部のKCDを0.3部のシリ
リル誘導体(S7D)に変えた他は、実施例34と同
様の操作をした時の結果を表12にまとめて示した。

【10104】実施例42

実施例34における0.5部のKCDを0.3部の7-
ニフテニル誘導体(C7D)に変えた他は、実施例34と同
様の操作をした時の結果を表12にまとめて示した。

【10104】実施例42

実施例34における0.5部のKCDを0.3部の7-
ニフテニル誘導体(C7D)に変えた他は、実施例34と同
様の操作をした時の結果を表12にまとめて示した。

【10104】実施例42

【10107】実施例45
実施例34における光重合開始剤系を、1. 5部のエオシニウム誘導体 (TPyD) に変えた他は、実施例34と同様の操作をした時の結果を表12にまとめて示した。

【10105】実施例43
実施例34における、5部のKCDを0. 3部のスズリウム誘導体 (SqD) に変え、また光源にHe-Neレーザ-の633nm光を使用した他は、実施例34と同様の方法で操作した時の結果を表12にまとめて示した。

【10106】実施例44
実施例34における、5部のKCDを0. 4部のスズニウム誘導体 (AzD) に変え、光源にHe-Neレーザ-の633nm光を使用した他は、実施例34と同様の方法で操作した時の結果を表12にまとめて示した。

【10109】
同様の方法で操作した時の結果を表12にまとめて示した。

【10108】実施例46
実施例34における光重合開始剤系を、1. 5部のスズニウム有機ホスホニウム誘導体 (AzB) に変え、Kイオンレーザ-の647nm光を使用した他は、実施例34と同様の方法で操作した時の結果を表12にまとめて示した。

【10109】
同様の方法で操作した時の結果を表12にまとめて示した。

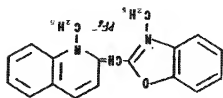
【10111】
同様の方法で操作した時の結果を表12にまとめて示した。

【10112】
同様の方法で操作した時の結果を表12にまとめて示した。

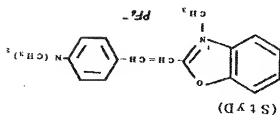
【10113】
同様の方法で操作した時の結果を表12にまとめて示した。

【10114】
同様の方法で操作した時の結果を表12にまとめて示した。

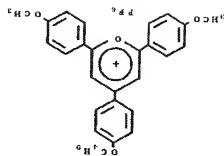
(24)



(CyD)



(StyD)

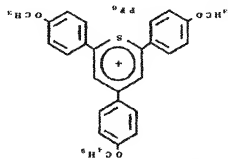


(PyD)

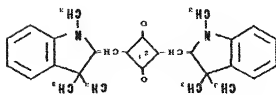
* * 【化7】

【0112】

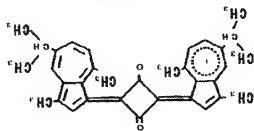
47 (TPYD)



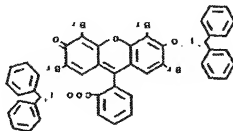
(SQD)



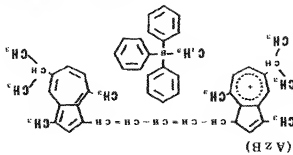
(AZD)



30 (E8)



(EY-DP1)



(AZB)

※50※実施例1における製造例1の7-メチル基を含有する高純

【0114】実施例47

【0113】

で、化学的安定性及び耐環境性に優れ、かつ高解像度、高回折効率を有する体積位相型ホログラムを製造することが可能となる。

【0117】

【図面の簡単な説明】

【図1】反射型ホログラム製造用の二光束レーザー露光装置のブロック図。

【図2】透過型ホログラム製造用の二光束レーザー露光装置のブロック図。

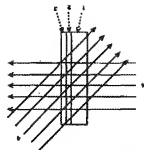
【図3】反射型ホログラム製造用の一光束レーザー露光装置のブロック図。

【0115】実施例4
【0116】実施例5

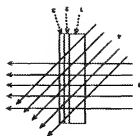
子重合体の粒子状分散液に換え、製造例2の7マシ原子を含む高分子重合体の粒子状分散液100部を用いた例は、実施例1と全く同様の方法でホログラムの作成を行った。感光膜の厚さが15 μ m、露光エネルギーが20mJ/cm²で、72%の回折効率（回折率実測値=0.0092）、486nmのブレイバグ波長を有する反射型ホログラムを得た。

【0115】実施例4
【0116】実施例5

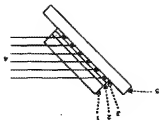
【発明の効果】本発明におけるホログラム用感光材料および該記録媒体の使用により、少ない露光エネルギー



【図1】



【図2】



【図3】

- 1: 基材 (ガラス板)
- 2: ホログラム記録用感光層
- 3: 保護フィルム (ポリエチレンフィルム)
- 4: スベシヤルツアルターを通して得られるコリマー
- 5: 反射ミラー (またはガラスホログラム)
- 6: ホログラム露光源

* NOTICES *

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.*** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the invention]

[0001]

[Industrial Application] This invention relates to the photosensitive materials for holograms and the hologram recording medium which were brought into the large wavelength area, are high sensitivity, and were excellent in chemical stability or an environmental capability-proof, and were excellent in resolution, diffraction efficiency, and transparency, and the manufacturing method of a hologram using it.

[0002]

[Description of the Prior Art] Since record of a three-dimensional stereoscopic model and reproduction are possible for a hologram, it is used for the display of covers, such as books and a magazine, POP, etc., the gift, etc., taking advantage of the outstanding design nature and the fanciness effect. Since the detailed information storage in a submicron unit is possible, it is applied to the mark for forgery prevention, such as negotiable securities, a credit card, and a prepaid card, etc. Since especially a volume phase type hologram becomes possible [modulating the light which passes the hologram formed by forming the spatial interference fringe from which a refractive index differs into a hologram recording medium], The application to the hologram optical element (HOE) represented by the scanner for POS and HUD (HUD) other than a display use is expected.

[0003] From the request to the volume phase type hologram on such industry, the proposal of the volume phase type hologram recording material using a photopolymer is made until now. For example, after exposing the hologram recording medium which consists of photopolymers to the interference pattern of a radiant ray as a manufacturing method of a hologram using a photopolymer, the method of performing the development by a developing solution is proposed. For example, in JP 62-22152, B, The sensitized material which combined the polyfunctional monomer and photopolymerization initiator which have two or more ethylenic

unsaturated bonds with the polymer which should turn into a carrier. The 1st process exposed to the interference pattern of a radiant ray, the 2nd process that processes this sensitized material with the 1st solvent, and makes this sensitized material swell. The 3rd process that processes with the 2nd scarce solvent of a swelling operation, and makes this sensitized material contract is provided, and the manufacturing method of the hologram using a photopolymer characterized by things is indicated. If the known art concerned is followed, can manufacture the hologram outstanding in points, such as diffraction efficiency, resolution, and an environmental capability-proof, but. Or it was inferior to a sensitivity characteristic and the sensitization wavelength area characteristic, it had a fault, like problems, such as a fall etc. of the manufacturing complicated nature of having adopted the wet process process in the manufacture of a hologram and the transparency by the development unevenness and the white bush mark resulting from the opening produced at the time of solvent immersion operation or a crack, arise.

[0004]The hologram recording material using the photopolymer which can manufacture a hologram only by interference exposure on the other hand as only down stream processing which does not need a complicated or complicated wet process process in the manufacturing process of a hologram, and its manufacturing method are indicated. For example, in U.S. Pat. No. 3,658,526, the photosensitive layer for hologram recording consisting of an aliphatic series polymer high polymer binder, an aliphatic series system acrylic monomer, and a photopolymerization initiator is proposed. in the art concerned, since the refractive index of the polymer and aliphatic series system acrylic monomer which are used was near, the range of the degree of refractive index modulation obtained by hologram exposure is 0.001 to 0.003, and, as a result, there was a fault that high diffraction efficiency was not acquired. In [that the technical problem in the art concerned should be solved] U.S. Pat. No. 4,942,112, Thermoplastic polymer of solvent fusibility and the boiling point A not less than 100 ° fluid ethylenic monomer, The photopolymerization nature constituent for hologram recording and the element for refractive-index pictures consisting of a solid ethylenic monomer and a photopolymerization initiator, in U.S. Pat. No. 5,098,803, Thermoplastic polymer, the substitution or unsubstituted phenyl, substitution, or unsubstituted naphthyl of solvent fusibility, The boiling point which it has substitution, an unsubstituted heterocycle group or a chlorine atom, and a bromine atom Or a not less than 100 ° fluid ethylenic monomer, And the photopolymerization nature constituent for hologram recording and the element for refractive-index pictures consisting of 0.005 or more is actually obtained, and things SPIE "Practical Holography IV", The 1212nd volume, 30 pages (1990) and "J of Imaging Science", the 35th volume, 19 pages, and 25 pages (1991) prove.

[0005]In these photopolymerization nature constituents for hologram recording, in order to

enlarge the degree of refractive index modulation produced in the exposure to the interference pattern of a radiant ray, Either polymer or a monomer is characterized by constituting from combination of the material which has a substituent containing an aromatic ring or a halogen atom, and (1) The thermoplastics of non-aromatic compound nature with an especially low refractive index. The so-called constituent of a monomer orientation type system which consists of combination with the fluid ethylenic acrylic monomer which has an aromatic group or a halogen atom is used suitably. As thermoplastic polymer of the non-aromatic compound (halogen) nature currently used in the art concerned, Poly methyl methacrylate, ethyl polymethacrylate, polyvinyl acetate, Polyacetic acid / acrylic acid vinyl, polyacetic acid / methacrylic acid vinyl, hydrolyzed type polyvinyl acetate, Ethylene/vinyl acetate copolymer, saturation and unsaturation polyurethane, butadiene, an isoprene polymer, and a copolymer, The polyethylene oxide which has an average molecular weight of 4,000 to 1,000,000. The EOKISHI ghost, N-methoxymethyl polyhexamethylene adipamide which have acrylate or a methacrylate group, Cellulose acetate, cellulose acetate succinate, cellulose acetate butyrate, In order to enlarge more the degree of refractive index modulation which are methyl cellulose, ethyl cellulose, a polyvinyl butyral, and a polyvinyl formal, and a refractive index is 1.46 or more and the all produce in the exposure to the interference pattern of a radiant ray. Smaller binder polymer of the refractive index was desired.

[0006] Usually, as polymer whose refractive index is lower than general-purpose thermoplastic polymer, in [the high molecular compound which has a fluorine atom is known well, and]

JP,3-50588,A and U.S. Pat. No. 4963471. The photopolymer nature constituent for holograms consisting of the fluid nature ethylenic unsaturated monomer and photoinitiator system which have a fluoride content polymer nature binder (a refractive index uses the thing of 1.42 to 1.45) of solvent solubility and the not less than 100 ° boiling point is proposed. In the art concerned, although it became possible to attain the high degree of refractive index modulation by using fluoride content polymer with a low refractive index, the concept applicable to the art using the polymer distributed to particle state without dissolving in a solvent used in this invention was not shown at all. In order to use the fluoride content polymers of solvent fusibility, chemical stability which the conventional fluoride system high molecular compound had, such as a solvent-proof and chemical resistance, will be sacrificed, but. Like this invention, it becomes possible by using the particle state polymers of solvent insolubility to aim at improvement in chemical stability.

[0007]

[Problem(s) to be Solved by the Invention] This invention provides the manufacturing method of a hologram using the photosensitive materials for holograms, the hologram recording medium, and it which crossed to the large wavelength area, are high sensitivity, and were excellent in chemical stability or an environmental capability-proof, and excellent in resolution, diffraction

efficiency, and transparency.

[0008]

[Means for Solving the Problem] This invention persons result in this invention, as a result of inquiring wholeheartedly in consideration of the above many points that the above-mentioned purpose should be attained. Namely, a polymer (A) in which this invention contains a fluorine atom, it consists of a solvent (D) which dissolves a compound (B) which has a functional group which can polymerize at least although a polymer (A) containing a photopolymerization initiator system (C) and a fluorine atom which are activated by exposure of a compound (B) and chemical action radiation which has a functional group which can polymerize is not dissolved, it distributes to particle state in a solution of a solvent (D) which dissolved a compound (B) which has a functional group in which a polymer (A) containing a fluorine atom can polymerize. They are the photosensitive materials for holograms which add a chain transfer agent (E) further to becoming photosensitive materials for holograms and these photosensitive materials for holograms, and are characterized by things, it is a hologram recording medium which carries out the stratification of these photosensitive materials for holograms on a substrate, and after [which twists this hologram recording medium to a laser beam] carrying out interference exposure, it is a manufacturing method of a hologram which has 0.005 or more refractive index modulation which performs exposure or heating by actinic rays. [Hereafter, this invention is explained extensively. A fluorine atom content polymer (A) currently first distributed on particles in [of use] a solvent (D) by this invention is explained. A polymer of such a gestalt A micro gel and polymers microsphere. A polymer generally named generically polymer particles, such as an emulsion or non AQUEOUS dispersion (NAD), is meant, and a unit which contains a fluorine atom especially in it means a polymer introduced by a certain method. For example, although a fluorine atom content polymer of organic solvent fusibility is used as dispersion stabilizer and a monomer is organic solvent soluble as a polymer which has such a gestalt, A monomer from which a polymer formed becomes insoluble can be used, and NAD etc. of a vinyl system polymer in which fluorine atom content polymers with good insolubility and dispersion stability were fixed by gel in this monomer in an organic solvent at a distributed registration bundle and this organic solvent can be shown. [0010] Fluorine atom content polymers which can be used in order to manufacture such NAD, Use a fluorocarbon as an essential ingredient and Alkyl vinyl ether, ant cyclic vinyl ether, it is a polymer of fusibility at an organic solvent which makes a copolymer component one sort or two sorts or more of unsaturated monomers chosen from hydroxyvinyl ether, an olefin, a halo olefin, unsaturated carboxylic acid, its ester, and carboxylic acid vinyl ester. Preferably, it is desirable for the weight average molecular weight to be 5,000 to 200,000, and for fluorine atom content to be 5 thru/or 70 % of the weight.

[0011] As a fluorocarbon in fluorine atom content polymers, tetrafluoroethylene,

chlorotrifluoroethylene, and vinyl fluorination, vinylidene fluoride, etc. are used. As alkyl vinyl ether which is other copolymer components, Ethyl vinyl ether, isobutylvinyl ether, n-butylvinyl ether, etc., As ant cyclic vinyl ether, cyclohexylvinyl ether and its derivative, As hydroxyvinyl ether, hydroxybutylvinyl ether etc., As an olefin and a halo olefin, ethylene, propylene, isobutylene, As carboxylic acid vinyl ester, VCM/PVC, a vinylidene chloride, etc. Vinyl acetate, As unsaturated carboxylic acid and its ester, n-butanoic acid vinyl ester. Acrylic acid (meta). Unsaturated carboxylic acid, such as crotonic acid, and (meta) methyl acrylate, (Meta) Ethyl acrylate, acrylic acid (meta) propyl, acrylic acid (meta) isopropyl, (Meta) The alkyl ester of C_6 acrylic acid (meta), such as butyl acrylate, acrylic acid (meta) hexyl, acrylic acid (meta) octyl, and acrylic acid (meta) lauryl, 18from C_{14} , hydroxyethyl (meta) acrylate, Hydroxy alkyl ester [of C_6 or acrylic acid (meta), such as hydroxypropyl (meta) acrylate, 8from C_{12}] and N, and N-dimethylaminomethyl (meta) acrylate, N,

and N-diethylaminomethyl (meta) acrylate etc. are mentioned. These radical polymerization nature monomer may be independent respectively, or it may be used for two or more sorts, combining. It may substitute for this a part of monomer if needed with vinyl compounds, such as other radical polymerization nature monomers, for example, styrene, alpha-methylstyrene, vinyltoluene, and acrylonitrile (meta). It is usable as other monomer derivatives in a fluoroolfin of carboxylic acid group content, glycidyl group content vinyl ether, etc.

[0012] Great-ization with a particulate material core part may be attained by introducing a polymerization nature double bond into such fluorine atom content polymers. As an introducing method of this polymerization nature double bond, a carboxylic acid group content monomer is used, for example as a copolymer component of fluorine atom content polymers, Although it can carry out by making a glycidyl group content unsaturated monomer, for example, glycidyl (meta) acrylate, allyl glycidyl ether, etc. react to this carboxyl group, it can carry out conversely also by making a glycidyl group content acrylic copolymer and a carboxyl group content unsaturated monomer react. Otherwise, such combination can consider an acid anhydride, a hydroxyl group and an acid anhydride, a sulfinyl group and an isocyanate group, a hydroxyl group, etc. General conditions from which an addition reaction occurs among such reactant group comrades are common knowledge, and conditions, such as temperature from which those reactions occur, can be changed according to a catalyst to be used. The above reactions enable it to introduce a polymerization nature double bond into fluorine atom content polymers. Although it is not indispensable in this invention to introduce a polymerization nature double bond into fluorine atom content polymers, by introducing a polymerization nature double bond. A covalent bond is formed between a polymer which forms particles, and fluorine atom content polymers which take charge of a function as dispersion stabilizer, and it becomes possible to aim at much more improvement in stability in inside of a solvent of a polymers dispersing

[0013] As an example of the fluorine atom content polymers, "Lumiflon" series (for example, Lumiflon LF200, weight average molecular weight: about 50,000, Asahi Glass Co., Ltd. make) of organic solvent fusibility which has a hydroxyl group, for example is mentioned. In addition, fluorine atom content polymers of organic solvent fusibility are marketed from Daikin Industries, LTD., Central Glass Co., Ltd., Penn Wall, etc., and these can also be used.

[0014] Manufacture of fluorine atom content polymers used in this invention is usually performed using a radical initiator. As an usable radical polymerization initiator, for example azobis(isobutyronitrile), Peroxide system initiators, such as azo initiators, such as 2 and 2'-azobis(2,4-dimethylvaleronitrile), benzoyl peroxide, lauryl peroxide, and tert-butyl peroxide, are mentioned. Generally as a reaction form, an emulsion polymerization in inside of an aqueous medium and solution polymerization in inside of an organic solvent are adopted. However, in use of these fluorine atom content polymers, it is used in the state where it is dissolved in an organic solvent, as dispersion stabilizer. As an organic solvent, it is usable in various solvents and usable in aromatic hydrocarbon, alcohols, ester species, ketone, and glycol ether. they use two or more sorts, these being independent or mixing them at a various rate -- straw mating can be carried out. Reaction temperature and reaction pressure are suitably chosen by a kind of polymerization initiator, a solvent kind, and reaction form.

[0015] At least one sort of radical polymerization nature monomers are made to polymerize in an organic fluid by making into dispersion stabilizer fluorine atom content polymers manufactured by the method in a polymer containing a fluorine atom which is used by this invention and which was distributed by particle state in a solvent. Although a distributed polymer particle generated by this polymerization does not dissolve substantially as an organic fluid used for this polymerization, An organic solvent of a fluorine atom content polymer solution which has the above-mentioned function as dispersion stabilizer, and a thing which has the function to maintain the dispersibility of a polymer conjointly generated to particle state are chosen. As an example of this organic fluid, aliphatic hydrocarbon, such as hexane, heptane, and octane, Aromatic hydrocarbon, such as benzene, toluene, and xylene, an alcohol system, An ether system, an ester system, and ketones, for example, isopropyl alcohol, Butyl alcohol, isobutyl alcohol, octyl alcohol, cellosolve, ethylene glycol monobutyl ether, methyl ethyl ketone, Methyl isobutyl ketone, diisobutyl ketone, ethyl acyl ketone, Even if methyl hexyl ketone, ethyl butyl ketone, ethyl acetate, isobutyl acetate, isomethyl acetate, acetic acid acyl, 2-ethylhexyl acetate, etc. are mentioned and it uses these alone, respectively, two or more sorts can be mixed and can also use, but. Generally aliphatic hydrocarbon is made into a subject and what combined aromatic hydrocarbon, an alcohol system like the above, an ether system, an ester system, or ketones with this suitably is used suitably. Trichlorofluoroethane, meta xylene hexafluoride, tetrachloro hexafluoro butane, etc. can be used as occasion

demands.

[0016] As a monomer made to polymerize by the bottom of existence of fluorine atom content polymers with a function as dispersion stabilizer described above and an organic fluid, if it is an unsaturated monomer of radical polymerization nature, there is no restriction in particular and various kinds of things can be used, but it will be as follows if the typical thing is illustrated.

(a) (meta) Acrylic ester; (meta) Methyl acrylate, (meta) Ethyl acrylate, acrylic acid (meta) propyl, acrylic acid (meta) isopropyl, (meta) Butyl acrylate, acrylic acid (meta) hexyl, acrylic acid (meta) octyl, (meta) Alkyl ester of C_4 of acrylic acid (meta), such as acrylic acid lauryl, thru/or C_{18} , Alkenyl ester of C_2 of acrylic acid (meta), such as glycidyl (meta) acrylate and allyl (meta) acrylate, thru/or C_8 . Hydroxy alkyl ester of C_2 of acrylic acid (meta), such as

hydroxyethyl (meta) acrylate and hydroxypropyl (meta) acrylate, thru/or C_8 . Alkenyloxy alkyl ester of C_3 of acrylic acid (meta), such as allyloxy ethyl (meta) acrylate, thru/or C_{18} , etc., Vinyl aromatic compound; (b) Styrene, alpha-methylstyrene, vinyltoluene, (c) alpha, such as p-KUROR styrene and vinylpyridine, beta-ethylenic unsaturated acid; (meta) acrylic acid and itaconic acid (d), others; (meta) Acrylonitrile, methyliso propenyl ketone, vinyl acetate, Vinyl propionate, vinyl pivalate, etc. are mentioned.

[0017] A polymerization of the above-mentioned monomer is performed using a radical initiator. As an usable radical polymerization initiator, 2 and 2-azo-isobutyro-dinitrile, Azo initiators, such as 2 and 2'-azobis (2,4-dimethylvaleronitrile), Peroxide system initiators, such as benzoyl peroxide, lauryl peroxide, and tert-butyl peroxoate, are mentioned, and, generally these polymerization initiators are used within the limits of 0.2 to 10 weight sections to monomer 100 weight section with which a polymerization is presented.

[0018] In manufacturing a polymer containing such a fluorine atom distributed by particle state in a solvent, it is convenient to use the amount of fluorine atom content polymers used with a function as the aforementioned dispersion stabilizer in 3 to 70% of the weight of the range to a total amount of a polymer which can be obtained. Concentration of a polymer containing a fluorine atom distributed by particle state in an organic fluid generally has 30 to 70% of the weight of a preferred range.

[0019] A range desirable as mean particle diameter of a polymer containing a fluorine atom used by this invention is 0.6 micrometer or less, and more desirable mean particle diameter is 0.2 micrometer or less. As the reason, are in charge of manufacturing a volume phase type reflection type hologram using a polymer of particle state in this invention. When carrying out two beam interference exposure with a parallel ray of laser shown in Drawing 1 and recording a diffraction pattern, an interval (d) of an interference fringe becomes narrow most, namely, that spatial frequency (resolution) becomes high. When both of the light flux enters in parallel

to a sensitive plate, it is at the time of conditions ($\theta_a=180$ degree and $\theta_R=0$ degree). In this case, d is computed by formula (A).

[0020]

$$d = \frac{\lambda}{2 \sin \left(\frac{\theta_a - \theta_R}{2} \right)} \quad \dots \text{式 (A)}$$

[0021]Here, it is $\theta_a=180$ degree and $\theta_R=0$ degree, and n shows the

general value 1.5 with a refractive index of a sensitization medium, and λ shows an oscillation wavelength (micrometer) of used laser. When the 441-nm light of helium-Cd laser of short wavelength is used for a laser light source, d is about 0.15 micrometer, and d is set to about 0.22 micrometer when the 676-nm light of Kr ion laser of long wavelength is used on the other hand. Therefore, in recording a pattern of such an interference fringe, it is desirable to use polymer particles which have particle diameter smaller than an interval of an interference fringe. It is also one of the reasons that light scattering may arise if particle diameter exceeds 0.8 micrometer from the wavelength range of 0.4 micrometer of visible light, and it may become causes, such as a white bluish mark.

[0022]Next, it illustrates about a compound (B) which has a functional group which can

polymerize use by this invention. A compound which has an ethylenic unsaturated bond which can polymerize as a functional group as such a compound, or a compound which has an oxirane ring which can be polymerized can be shown. As a compound which has in detail an ethylenic unsaturated bond which can polymerize, A compound which has an acrylyl group or an allyl group (meta) which can carry out addition condensation with a free radical by which it is generated from a photoinitiator system in an operation of chemical action, A compound which has a vinyl ether group which can carry out addition condensation with acid (Lewis) by which it is generated from a photoinitiator system in an operation of chemical action (Lewis) can be mentioned. An epoxy compound which can carry out cationic polymerization as a compound which has an oxirane ring which can polymerize with acid (Lewis) by which it is generated from a photoinitiator system in an operation of chemical action can be

mentioned.

[0023]In this invention, in order for interference exposure of a laser beam to attain the degree of refractive index modulation of 0.005 or more, it is important to devise suitably combination of a polymer which has a fluorine atom, and a compound which has a functional group which can be polymerized, and creating a hologram which has high diffraction efficiency by it begins, and it becomes possible. It is possible to specifically build combination shown below. that is, (1) A

fluorine atom. A combination (2) fluorine atom of a polymer and (1) which it has. A combination (3) fluorine atom of a polymer and (11) which it has. Compound chosen from a polymer which has a combination (4) fluorine atom of a polymer and (111) which it has, a polymer which has a combination (5) fluorine atom, (1V), (1), or (1V) A combination (6) fluorine atom with arbitrary mixtures. a polymer which it has, and compound chosen from (1) or (11) . (VI) a polymer which has a combination (7) fluorine atom, and ** chosen from (111) or (1V) combination of *** and (V) -- here, (1) thru/or (V), (1) Inside of a compound which has an ethylenic unsaturation group which can polymerize, non halogen system aliphatic series combination inside of a compound which has an ethylenic unsaturation group and a sulfur atom in which a thing (11) compounds which have an ethylenic unsaturation group in which an aliphatic compound (111) polymerization is possible, and in which a compound (1V) polymerization is possible, intramolecular -- a sulfur atom -- and -- Among compounds which have an oxirane ring which has an aromatic ring or (and) a halogen atom, and in which a compound (V) polymerization is possible, Although a compound etc. which have an aromatic ring or (**) a halogen atom in intramolecular among compounds which have an oxirane ring in which a non halogen system aliphatic series system compound (VI) polymerization is possible can be shown, If it is the combination of a presentation which can attain the degree of refractive index modulation of 0.005 or more, it will not be limited to these. Hereafter, these compounds are illustrated in detail.

[0024]First, a non halogen system aliphatic series system compound is illustrated among compounds which have an ethylenic unsaturation group which can polymerize. As a monofunctional type, specifically Unsaturated acid compounds, such as acrylic acid (meta), itaconic acid, and maleic acid, Methyl (meta) acrylate, ethyl (meta) acrylate, n-butyl (meta) acrylate, t-butyl (meta) acrylate, isobutyl (meta) acrylate, Isoamyl (meta) acrylate, 2-ethylhexyl (meta) acrylate, 2-hydroxyethyl (meta) acrylate, 2-hydroxypropyl (meta) acrylate, 2-hydroxybutyl (meta) acrylate, 2-ethoxyethyl (meta) acrylate, 2-(2-ethoxyethoxy) ethyl (meta) acrylate, n-butoxyethyl (meta) acrylate, morpholino ethyl (meta) acrylate, Which alkyl (meta) acrylate type, methoxy JIECHI (PURORI) RENGU recall (meta) acrylate, Methoxy TORIECHI (PURORI) RENGU recall (meta) acrylate, Methoxy acrylate, TETORAECHI (PURORI) RENGU recall (meta) acrylate, methoxy polyethylene (PURORI) RENGU recall (meta) acrylate, JIECHI (PURORI) RENGU recall (meta) acrylate, ethoxy JIECHI (PURORI) RENGU recall (meta) acrylate, Ethoxy TORIECHI (PURORI) RENGU recall (meta) acrylate, Alkoxy alkylene glycol (meta) acrylate types, such as ethoxy polyethylene (PURORI) RENGU recall (meta) acrylate, Cyclohexyl (meta) acrylate, tetrahydro furil (meta) acrylate, isobornyl (meta) acrylate, dicyclopentaniil(metha)acrylate, Tricyclo penta nil (meta) acrylate, dicyclopentadienyl (meta)

acrylate, Allylic (meta) acrylate types, such as Pina Nils (meta) acrylate, N and N-dimethylaminoethyl (meta) acrylate, N, and N-diethylaminoethyl (meta) acrylate, (Meta) functional group content (meta) acrylate, such as amine type (meta) acrylate, such as acrylamide and diacetone (meta) acrylamide, allyl (meta) acrylate, and glycidyl (meta) acrylate, etc. are mentioned.

[0025]As a polyfunctional mold, next, 1, 3-pro pansy ORUli (meta) acrylate, 1, 4-butanediol di(metha)acrylate, 1, 5-hexanediol di(metha)acrylate, Neopentyl glycol di(metha)acrylate, a bis(acryloxy neopentyl glycol)horse mackerel pear, A bis(meta-KURIRORIKISHI neopentyl glycol) horse mackerel pear, epichlorohydrin denaturation 1, 5-hexanediol di(metha)acrylate : Nippon Kayaku Kaya Rudd R-167, hydroxy pivalate neopentyl glycol di(metha)acrylate, Caprolactone denaturation hydroxy pivalate neopentyl glycol di(metha)acrylate : Alkyl type (meta) acrylate, such as Nippon Kayaku Kaya Rudd HX series, Ethylene glycol di(metha)acrylate, diethylene glycol di(metha)acrylate, Tetraethylene glycol di(metha)acrylate, tetraethylene glycol di(metha)acrylate, poly ethylene glycol di(metha)acrylate, epichlorohydrin denaturation ethylene glycol di(metha)acrylate : Nagase DENAKORU DA(M)-811, Epichlorohydrin denaturation glycol di(metha)acrylate : Nagase DENAKORU DA(M)-851, propylene glycol di(metha)acrylate, Dipropylene GURIKORUJI (meta) acrylate, Tori propylene glycol di(metha)acrylate, Tetra propylene glycol di(metha)acrylate, poly propylene glycol di(metha)acrylate, Epichlorohydrin denaturation pro RENGURIKORUJI (meta) acrylate : Alkylene glycol type (meta) acrylate, such as Nagase DENAKORU DA(M)-911, TORIMECHI roll pro pantry (meta) acrylate, diftrimethylol pro pantry (meta) acrylate, A neopentyl glycol denaturation TORIMECHI roll pro pansy, (Meta) Acrylate : Nippon Kayaku Kaya Rudd R-604, ethyleneoxide denaturation TORIMECHI roll pro pantry (meta) acrylate:Sartomer SR-454, PFA-310 by propylene oxide denaturation TORIMECHI roll pro pantry (meta) acrylate:Nippon Kayaku, Epichlorohydrin denaturation TORIMECHI roll pro pantry (meta) acrylate : Trimethylolpropane type (meta) acrylate, such as Nagase DA(M)-321, Penta ERIS RITORUTORI (meta) acrylate, pentaerythritol tetra (meta) acrylate, Stearic acid denaturation pentaerythritol di(metha)acrylate : Toagosei ARONIKKUSU M-233, dipentaerythritol hexa (meta) acrylate, Dipentaerythritolmonohydroxy penta (meta) acrylate, Alkyl modification dipentaerythritol poly (meta) acrylate : Nippon Kayaku Kaya Rudd D-310,320,330 etc., Caprolactone denaturation dipentaerythritol poly (meta) acrylate : Pentaerythritol type (meta) acrylate, such as Nippon Kayaku Kaya Rudd DPCA-20, 30, 60, 120, GURISERORUJI (meta) acrylate, epichlorohydrin denaturation glycerol RUTORI (meta) acrylate : Glycerol type (meta) acrylate, such as Nagase DENAKORU DA(M)-314 and triglycerol di(metha)acrylate, JISHIKUROROPENTANIRUJI (meta) acrylate, Tricyclo penta NIRUJI (meta) acrylate, cyclo HEKISHIRUJI (meta) acrylate, Methoxy-ized cyclo HEKISHIRUJI (meta) acrylate : Alicyclic (meta) acrylate, such as Sanyo-Kokusaku Pulp CAM-200, Tfs (acryloxyethyl) isocyanurate : Toagosei ARONIKKUSU M-315, tfs

(methacryloxyethyl) isocyanurate, isocyanurate type (meta) acrylate, such as caprolactone denaturation tris (acryloxyethyl) isocyanurate and caprolactone denaturation tris (methacryloxyethyl) isocyanurate, etc. are mentioned.

[0026] A compound which contains a sulfur atom in intramolecular further among compounds which have an ethylenic unsaturation group which comprises only an aliphatic group, and which can be polymerized is illustrated. As a monofunctional type, for example, methoxy JIECHI (PUROP) RENGU recall thio (meta) acrylate, Methoxy TETORAECHI (PUROP) RENGU recall thio (meta) acrylate, Methoxy TORIECHI (PUROP) RENGU recall thio (meta) acrylate, Methoxy polyethylene (PUROP) RENGU recall thio (meta) acrylate, Ethoxy JIECHI (PUROP) RENGU recall thio (meta) acrylate, Ethoxy TORIECHI (PUROP) RENGU recall thio (meta) acrylate, Alkoxy alkylene glycol thio (meta) acrylate types, such as ethoxy polyethylene (PUROP) RENGU recall thio (meta) acrylate, Cyclohexylthio (meta) acrylate, tetrahydro furil thio (meta) acrylate, isobornyl thio (meta) acrylate, dicyclopentaniil thio (meta) acrylate, Alicyclic thio (meta) acrylate types, such as tricyclo penta nil thio (meta) acrylate, dicyclopentadienyl thio (meta) acrylate, and PINANIRUCHIO (meta) acrylate, etc. are mentioned.

[0027] As a polyfunctional mold, next, 1, 3-pro pansy ORUICHIO (meta) acrylate, 1,4-butanediol dithio (meta) acrylate, 1,5-hexanediol dithio (meta) acrylate, Neopenyl glycol dithio (meta) acrylate, 1-bis(thio acryloyl neopenyl glycol)horse mackerel peat, A bis(thio meta-KURIROKISHI neopenyl glycol)horse mackerel peat, epichlorohydrin denaturation 1,6-hexanediol dithio (meta) acrylate, Hydroxy pivalate neopenyl glycol dithio (meta) acrylate, Alkyl type thio (meta) acrylate, such as caprolactone denaturation hydroxy pivalate neopenyl glycol dithio (meta) acrylate, Ethylene glycol dithio (meta) acrylate, diethylene-glycol dithio (meta) acrylate, Triethylene glycol dithio (meta) acrylate, Tetraethylene glycol dithio (meta) acrylate, Polyethylene-glycol dithio (meta) acrylate, epichlorohydrin denaturation ethylene glycol dithio (meta) acrylate, epichlorohydrin denaturation diethylene-glycol dithio (meta) acrylate, Propylene glycol dithio (meta) acrylate, dipropylene glycol dithio (meta) acrylate, Tetrapropylene glycol dithio (meta) acrylate, Tripropylene glycol dithio (meta) acrylate, such as polypropylene-glycol dithio (meta) acrylate and epichlorohydrin denaturation pro RENGU recall dithio (meta) acrylate, Trimethylopropane TORICHIO (meta) acrylate, difmethylo pro pantry thio (meta) acrylate, Neopenyl glycol denaturation trimethylopropanedithio (meta) acrylate, Ethyleneoxide denaturation trimethylopropane TORICHIO (meta) acrylate, Propylene oxide denaturation trimethylopropane TORICHIO (meta) acrylate, Trimethylopropane type thio (meta) acrylate, trimethylopropane TORICHIO (meta) acrylate, Trimethylopropane type thio (meta) acrylate, Stearic acid denaturation pentaerythritol hexathio (meta) acrylate, Dipentaerythritol hexathio (meta)

acrylate, dipentaerythritolmonohydroxy pentaithio (meta) acrylate, Alkyl modification dipentaerythritol polythio (meta) acrylate, Pentaerythritol type thio (meta) acrylate, such as caprolactone denaturation dipentaerythritol polythio (meta) acrylate, Glycerol dithio (meta) acrylate, epichlorohydrin denaturation glycerol TORICHIO (meta) acrylate, Glycerol type thio (meta) acrylate, such as triglycerol dithio (meta) acrylate, Dicyclopentanil dithio (meta) acrylate, tricyclo penta nil dithio (meta) acrylate, Allicyclic thio (meta) acrylate, such as cyclohexyldithio (meta) acrylate and methoxy-ized cyclohexyldithio (meta) acrylate, Tris (thio acryloxyethyl) isocyanurate, tris (thio methacryloxyethyl) isocyanurate, caprolactone denaturation tris (thio acryloxyethyl) isocyanurate, tris (thio methacryloxyethyl) isocyanurate, such as caprolactone denaturation tris (thio methacryloxyethyl) isocyanurate, etc. are mentioned. It may be independent, or more than one may be mixed, and these may be used.

[0028]As a compound which has an aromatic ring or (and) a halogen atom in intramolecular among compounds which have an ethylenic unsaturation group, Styrene, such as styrene, alpha-methylstyrene, and 4-ME (d) TOKISHI styrene. Phenyl (meta) acrylate, 4-phenylethyl (meta) acrylate, 4-methoxy carbonylphenyl (meta) acrylate, 4-ethoxycarbonylphenyl (meta) acrylate, 4-butoxycarbonylphenyl (meta) acrylate, Benzyl (meta) acrylate, phenoxy (meta) acrylate, Phenoxy hydroxypropyl (meta) acrylate, 4-phenoxylethyl (meta) acrylate, 4-phenoxydiethylene glycol (meta) acrylate, 4-phenoxyltetraethylene glycol (meta) acrylate, 4-phenoxyhexaethylene glycol (meta) acrylate, EO denaturation phenoxy-ized phosphoric acid (meta) acrylate, EO denaturation phthalic acid (meta) acrylate, 4-biphenyl (meta) acrylate, an aromatic polyhydroxy compound, for example, hydrotquinone, resorcinol, catechol, dl, such as pyrogallol, or a poly (meta) acrylate compound, bisphenol A di(meth)acrylate, ECHI (PURORI) RENOKI side denaturation bisphenol A di(meth)acrylate, Bisphenol F di(meth)acrylate, ECHI (PURORI) RENOKI side denaturation bisphenol F di(meth)acrylate, Bisphenol S di(meth)acrylate, ECHI (PURORI) RENOKI side denaturation bisphenol S di(meth)acrylate, An acrylate compound which has aromatic groups, such as epichlorohydrin denaturation phthalic acid di(meth)acrylate (meta), p-chlorostyrene, p-bromostyrene, p-chlorophenoxyethyl (meta) AKURETO, p-bromophenoxyethyl (meta) AKURETO, trichloro FENORUECHI (PURORI) RENOKISHIDO denaturation (meta) acrylate, Tribromo FENORUECHI (PURORI) RENOKISHIDO denaturation (meta) acrylate, tetrachlorobisphenol A ECHI (PURORI) RENOKISHIDO denaturation di(meth)acrylate, tetrachlorobisphenol A ECHI (PURORI) RENOKISHIDO denaturation di(meth)acrylate, Tetrachlorobisphenol S ECHI (PURORI) RENOKISHIDO denaturation di(meth)acrylate, the styrene which has the aromatic group replaced with a halogen atom with an atomic weight more than chlorine, such as tetrabromo bisphenol S ECHI (PURORI) RENOKISHIDO

denaturation di(meth)acrylate, and (meta-) an acrylate compound. A vinyl compound which has hetero aromatic groups, such as N-vinylcarbazole and 3-ME (d) ****, N-vinylcarbazole, 3-

chloro-2-hydroxypropyl (meta) acrylate, 3-bromo-2-hydroxypropyl (meta) acrylate, An acrylate compound (meta) etc. which were replaced with halogen atoms, such as 2,3-dichloropropyl (meta) acrylate, 2, and 3-dibromopropyl (meta) acrylate, are mentioned.

[0029] To intramolecular as an aromatic ring or (and) a halogen atom, and a compound that has a sulfur atom further at intramolecular, Phenylthio (meta) acrylate, 4-phenylethyl thio (meta) acrylate, 4-carbomethoxy phenylthio (meta) acrylate, 4-ethoxycarbonyl phenylthio (meta) acrylate, 4-butoxycarbonyl phenylthio (meta) acrylate, 4-tert-butyl phenylthio (meta) acrylate, Benzylthio (meta) acrylate, 4-phenoxydiethylene glycol thio (meta) acrylate, 4-biphenylthio (meta) acrylate, an aromatic polyhydroxy compound, For example, dithio or polythio (meta) acrylate compounds, such as hydroquinone, resorcinol, catechol, and pyrogallol, Bisphenol A dithio (meta) acrylate, ECH1 (PUR0P1) RENOKI side denaturation bisphenol A dithio (meta) acrylate, Bisphenol F dithio (meta) acrylate, Bisphenol S dithio (meta) acrylate, RENOKI side denaturation bisphenol F dithio (meta) acrylate, ECH1 (PUR0P1) RENOKI side denaturation bisphenol A dithio (meta) acrylate, Bisphenol A dithio (meta) acrylate, Bisphenol S dithio (meta) acrylate, A thio (meta) acrylate which have the aromatic group replaced with a halogen atom with an atomic weight more than chlorine, such as tetrabromo bisphenol S ECH1 (PUR0P1) RENOKISHIDO denaturation dithio (meta) acrylate, Tetraclorobisphenol A ECH1 (PUR0P1) RENOKISHIDO denaturation dithio (meta) acrylate, Tetraclorobisphenol A ECH1 (PUR0P1) RENOKISHIDO denaturation thio (meta) acrylate, Tribromo FENORUECH1 (PUR0P1) RENOKISHIDO denaturation thio (meta) acrylate, Trichloro FENORUECH1 (PUR0P1) RENOKISHIDO phthalic acid dithio (meta) acrylate, 3-chloro FENORUECH1 (PUR0P1) RENOKISHIDO denaturation thio (meta) acrylate, Tetraclorobisphenol A ECH1 (PUR0P1) RENOKISHIDO denaturation dithio (meta) acrylate, 2,3-dichloropropylthio (meta) acrylate, are mentioned.

[0030] A compound which polymerizes through ring breakage sigma bond cleavage as a compound which has an ethylenic unsaturated bond and in which addition condensation is possible is also mentioned. Such a compound A volume KJ, Ivin and on T. SAEUSA, Elsevier, New York, Chapter 1 of 1984 "General Thermodynamics andMechanistic Aspects ofRing-Opening Polymerization" -- the 1st page - the 82nd page, and chapter 2 "Ring Opening Polymerization via Carbon-Carbon Sigabond Cleavage" -- the 83rd page - the 19th page, W. J. J. Macromol. Sci.-Chem. of Bailey and others, A21 volume, J. Polym. Sci. of the 161st page - the 1639th page, 1984, I. Cho, and K-D. Ahn, and Polym. Lett. Ed. -- it is indicated in the 15th volume, the 751st page - the 753rd page, and 1977. As an example, vinylcyclopropane,

for example, 1,1-dichloro-2-vinylcyclopropane, the diethyl 2-vinylcyclopropane 1, 1-dicarboxylate (EVCD), Ethyl-1-acetyl-2-vinyl-1-cyclopropane carboxylate (EAVC), ethyl-1-benzoyl-2-vinyl-1-cyclopropane carboxylate (EBVC), etc. are mentioned. It may be independent, or more than one may be mixed, and these may be used, and it may mix with the aforementioned (meta) acrylic compound or a vinyl compound, and they may use.

[0031] Although the above compound is a compound which can carry out addition condensation with a free radical by which it is generated from a photoinitiator system in an operation of a chemical action line, A compound which has not a radical polymerization but an ethylenic unsaturated bond which can carry out cationic polymerization with acid (Lewis) by which it is generated from a photoinitiator system can also be illustrated. For example, a compound containing a vinyl ether group which can polymerize as such a compound can be mentioned. As a concrete vinyl ether compound, for example Ethylene GURIGORU divinyl ether, Ethylene glycol monovinyl ether, propylene glycol divinyl ether, glycerol divinyl ether, Glycero RUTORI vinyl ether, trimethylolpropanemonovinyl ether, Trimethylolpropanedivinyl ether, trimethylolpropane TORIBI nil ether, a jig -- a lycee -- RORUTORI vinyl ether and sorbitol tetra(vinyl ether, Allyl vinyl ether, 2,2-bis(4-cyclohexanoyl)propane divinyl ether, 2,2-bis(4-cyclohexanoyl)trifluoropropane divinyl ether, 4-vinyl ether styrene, hydroquinone divinyl ether, and phenylvinyl ether, Bisphenol A divinyl ether, p-tetrabromobisphenol A divinyl ether, bisphenol F divinyl ether, phenoxyethylene vinyl ether, bromophenoxyethylene vinyl ether, A compound which has a vinyl ether group by alkyl vinyl ether, such as which aryl ether and tert-butylvinyl ether, can be mentioned.

[0032] Next, an epoxy compound of an aliphatic series system is explained among compounds containing an oxirane ring which can polymerize. For example, ethylene glycol diglycidyl ether, ethylene glycol monoglycidyl ether, Propylene glycol diglycidyl ether, propylene glycol monoglycidyl ether, Neopenlyl glycol diglycidyl ether, neopenlyl glycol monoglycidyl ether, Glycero diglycidyl ether, GURUSE roll triglycidyl ether, Trimethylolpropane diglycidyl ether, trimethylolpropane monoglycidyl ether, trimethylolpropane triglycidyl ether and a jig -- a lycee -- roll triglycidyl ether. Sorbitol tetraglycidyl ether, allyl glycidyl ether, 2-ethylhexyl glycidyl ether, vinylcyclohexene dioxide, 3,4-epoxycyclohexylmethyl 3,4-epoxy cyclohexene carboxylate, A bis(3,4-epoxycyclohexyl)horse mackerel peel, a bis(3,4-epoxy-6-methylcyclohexylmethyl)horse mackerel peel, 2,2-bis(4-(2,3-epoxy propoxy) cyclohexyl) propane, 2,2-bis(4-(2,3-epoxy propoxy) cyclohexyl) hexafluoropropane etc. can be mentioned.

[0033] An epoxy compound which has an aromatic ring or (and) a halogen atom among compounds containing an oxirane ring which can polymerize is explained. For example, styrene oxide, p-bromostyrene oxide, phenyl glycidyl ether, Bisphenol A-diglycidyl ether,

tetrapromobisphenol A-diglycidyl ether, bisphenol F-diglycidyl ether, 2-phenylethylene oxide, etc. can be mentioned.

[0034]Next, if it exposes to actinic rays used by this invention, a photopolymerization initiator system (C) which activates a polymerization of a compound (B) which has a functional group which can polymerize will be illustrated. By an interaction of at least one sort of sensitizer (b) which has absorption in a wavelength area over near-infrared rays as such a photopolymerization initiator system from ultraviolet, and sensitizer (b) exposed by active radiation. A compound system with which at least one sort of mixed stock or a sensitizer of initiator (**) which generates active species which induces a polymerization of a compound (B) which has one or more functional groups which can polymerize, and an initiator were united by ionic bond or a covalent bond can be mentioned.

[0035]The unsaturated ketone represented by a chalcone derivative, dibenzal acetone derivative, etc. as an example of sensitizer (b), for example, 1, 2-diketone derivative in which benzyl, camphor quinone, etc. are represented, A benzoin derivative, a fluorene derivative, a naphthoquinone derivative, an anthraquinone derivative, A xanthene derivative, a thioxanthene derivative, a xanthone derivative, A coumarin derivative, A keto cyanine coumarin derivative, a thio keto coumarin derivative, a cyanine derivative, A keto cyanine derivative, a merocyanine derivative, an oxo Nord derivative, a styryl derivative, An acridine derivative, an azine derivative, a thiazine derivative, an oxazine derivative, An indoline derivative, an azlucine derivative, an AZURENINIUM derivative, a SUKUWARIRIUM derivative, A porphyrin derivative, a tetra benzoporphyrin derivative, a tetranaphthopoly FIRIN derivative, A porphyrin derivative, a tetra methane derivative, a tetraaza porphyrin derivative, and a

phthalocyanine derivative. A naphthalocyanine derivative, a tetraaza porphyrine derivative, a tetrapyrazino porphyrazine derivative, a tetra kino KISARIRO porphyrazine derivative, the The Rafi Lynne derivative, an annulene derivative, a pyrillium derivative, a thio pyrillium derivative, They are mentioned by a pyran derivative, a spiro pyran derivative, a spiro oxazine derivative, a thiospiro pyran derivative, organic ruthenium complex, etc., and to others. Furthermore, volumes for Shin Ogawara, a "coloring matter handbook" (1986, Kodansha), Volumes for Shin Ogawara, "chemicals of functional dye" (1981, CMC), Coloring matter and a sensitizer given in volumes on Tadashi ikemori 3 **, and "special function material" (1986, CMC), U.S. Pat. No. 3,652,275, U.S. Pat. No. 4,162,162, U.S. Pat. No. 4,268,667, U.S. Pat. No. 4,351,893, U.S. Pat. No. 4,454,218, U.S. Pat. No. 4,535,052, JP,2-85858A, JP,2-216154A, A compound which has absorption in wavelength of radiant rays, such as an unsaturation ketone system sensitizer of a statement, is mentioned to JP,5-27436A. These sensitizer (b)s may be used as two or more sorts of mixtures by arbitrary ratios if needed. In the case of anionic dyestuff like a xanthene derivative among these sensitizer (b)s, a thioxanthene derivative, or an oxo Nord derivative, An aryl diazonium cation, a diaryl iodonium cation, A triarylsulfonium cation, a

dialkyl phenacyl sulfonium cation, an alkyl aryl phenacyl sulfonium cation, May be the compound in which onium cations, such as an alkyl aryl phenacyl sulfonium cation, a diaryl phenacyl sulfonium cation, or a diaryl phenacyl sulfoxonium cation, carried out the ionic bond, and, on the other hand, a cyanine derivative, a case of a cationic color like an AZURENINIUM derivative, a pyrilium derivative, or a thio pyrilium derivative -- doria -- a compound which carried out the ionic bond may be sufficient as organic boric acid anions, such as a real alkyl boron anion.

[0036]Next, a compound shown below can be illustrated as initiator (**). For example, annular ***- - alpha-dicarbonyl compounds, such as 2,3-borane dione (camphor quinone) and 2,2,5,5-tetramethyl tetrahydro 3,4-franc acid (imidazotetrone), Benzophenone, diacetyl, benzyl, MIHIRAZU ketone, a dieethoxyacetophenone, ketone, such as 2-hydroxy-2-methylpropiohenone and 1-hydroxycyclohexylphenyl ketone. Peroxides, such as benzoyl peroxide and di-tert-butyl peroxide, Aromatic carboxylic acid, such as diazonium salt, such as aryl diazonium, and N-phenylglycine, Xanthenes, such as 2-chloro thioxanthene and a 2,4-diethylthio xanthene. Diaryliodonium salt, sulfonium salt, triphenyl alkyl borate salt, a metal arene complex, screw imidazole derivatives, a poly halogenated compound, phenylisoxazoline, benzoin ethyl ether, benzyl dimethyl ketal, etc. are raised. These photopolymerization initiator systems (C) may be used as two or more sorts of mixtures by arbitrary ratios if needed. When a compound (B) which has especially one or more functional groups which can polymerize use by this invention has a different functional group in the intramolecular, or to mix and use a compound which has a different functional group, it is necessary to choose a photopolymerization initiator system according to those functional groups suitably.

[0037]As a desirable photopolymerization initiator, 2, such as British JP, 1388492,B and given in JP,53-133428,A tris (trichloromethyl)-2, 4, and 6-triazine, 4, 6-substitution triazine compound, Organic peroxide, such as JP,59-189340,A and 3,3',4,4'-tetra(tert-butylperoxy carbonyl) benzophenone given in JP,60-76503,A, JP,1-54440,A, the European Patent No. 109851, the European Patent No. 126712, and "a Journal OBU imaging science (J. Imag.Sci.), The 30th volume, an iron arene complex given in the 174th page (1986), diphenyliodonium hexafluorophosphate, Diaryliodonium salt, such as JI (p-tolyl) iodonium hexafluorophosphate and diphenyliodoniumhexafluoroantimonate, Triphenylsulfoniumhexafluorophosphate, diphenylphenacyl sulfoniumhexafluoroantimonate, dimethylphenacyl sulfonium hexafluorophosphate, Sulfonium salt, such as benzyl-4-hydroxy phenylmethyl sulfoniumhexafluoroantimonate, Oxo sulfonium salt, such as TETORAFENIRU oxo sulfonium hexafluorophosphate, Iodonium or organically boron complexes, such as diphenyliodonium (n-butyl) triphenyl borate given in JP,3-704,A, Diphenylphenacyl sulfonium (n-butyl) triphenyl borate given in JP,5-255347,A, Sulfonium organically boron complexes, such as

dimethylphenacyl sulfonium (n-butyl) triphenyl borate given in JP,5-213861,A. An iron arene organicity boron complex "ORUGANOMETARIKKUSU (Organometallics)", the 8th volume, and given in the 2737th page (1989) etc. are mentioned.

[0038]Especially A trihalomethyl substitution-triazine compound, an iron arene complex, arene diazonium salt, Photopolymerization initiators, such as diaryliodonium salt, a triarylsulfonium salt, and dialkyl phenacyl sulfonium salt, can generate both a radical and acid by an interaction with a sensitizer in a photoexcited state.

[0039]Next, a chain transfer agent (E) of use by this invention is effective in order to raise diffraction efficiency of a hologram. As a desirable chain transfer agent, are thiols, and For example, 2-mercapto Benz oxazole, 2-mercapto Benz thiazole, 2-mercapto Benz imidazole, 4,4'-Thiobis benzenethiol, p-bromobenzenethiol, Thiocyanuric acid, 1,4-bis(mercaptomethyl) benzene, p-toluene thiol, etc., This is given [USP / No. 4414312] in JP,64-13144,A, Disulfide given in JP,2-291561,A, thione given [USP / No. 3558322] in JP,64-17048,A, O-acyl thiohydronallium KISAMETO given in JP,2-291560,A and N-alkoxy pyridinethione, etc. are mentioned. The amount of chain transfer agent used has 1.0 - 30 preferred weight section to polymer (A) 100 weight section containing a fluorine atom.

[0040]Photosensitive materials for holograms of this invention to dispersion liquid of a polymer (A) which contains in a solvent a fluorine atom distributed to particle state. The mixture solution of a compound (B) which has one or more functional groups in which a photopolymerization initiator system (C), (sensitizer ("*, and initiator ("*,)) and a polymerization are possible, and also the chain transfer agent (E) is carried out, and it is used. Although there is no specific restriction in a compounding ratio of each above-mentioned ingredient, it is preferred to prepare concentration of a sensitizer so that transmissivity of light emitted from a light source with which an exposure is presented may be 1% or more. It is possible to add thermal polymerization inhibitor to photosensitive materials for holograms of this invention, in order to prevent a polymerization at the time of preservation. As an example, p-methoxy phenol, hydroquinone, alkylation hydroquinone, Catechol, tert-butylcatechol, phenothiazin, etc. can be raised and, as for these thermal polymerization inhibitors, it is preferred to be added in the range of 0.001 to 5 weight sections to compound 100 weight section which has an ethylenic unsaturated bond. [0041]According to the purpose, it may be further used for photosensitive materials for holograms of this invention, mixing with deoxidizers, such as phosphine, phosphonate, and phosphite, a reducing agent, an antihalation agent, a plasticizer, a leveling agent, an ultraviolet ray absorbent, a spray for preventing static electricity, etc. to them. Mixed use of the amines, such as triethanolamine, N,N-diethylaniline, and N-phenylglycine, may be carried out as an additive agent for promotion of a polymerization.

[0042]Among photosensitive materials for holograms of this invention, quantity occupied in photosensitive materials for holograms of a polymer (A) containing a fluorine atom except for a

solvent is 30 to 70 % of the weight preferably ten to 90% of the weight, in order to manufacture high diffraction efficiency, high resolution, and a hologram that has high transparency. The

amount of compound (B) used which has a functional group which can polymerize is 40 - 150 weight section preferably ten to 200 weight section to polymer (A) 100 weight section. [0043]Sensitizer (**) is preferably used in the range of 0.5 - 15 weight section 0.1 to 30 weight section to polymer (A) 100 weight section containing a fluorine atom among

photopolymerization initiator systems (C) used with photosensitive materials for holograms of this invention. The amount used receives restriction with optical density of photosensitive layer thickness and this thickness. That is, it is preferred that optical density uses it in the range which does not exceed 2. Initiator (**) is preferably used in the range of 1 - 15 weight section 0.1 to 20 weight section to polymer (A) 100 weight section containing a fluorine atom.

[0044]On a substrate, an obtained sensitizing solution is applied in the shape of a coat, and is used as a recording medium for holograms. Although it is preferred to use 50 micrometers from 1 micrometer as thickness after desiccation as for thickness applied and the range of 4 to 20 micrometers is more preferred, the thickness, Relation between hologram demand characteristics, such as diffraction efficiency or regenerated light half breadth, and the degree of refractive index modulation (delta) or a hologram manufactured needs to set it as optimal thickness by any of a reflection type hologram or a transmission type hologram. The rationale is indicated by Bell,Syst.Tech.J. of H.Kogelnik work, the 48th volume, and the 2908th page (1969).

[0045]As a substrate, a glass plate, a polymethylmethacrylate board, a polycarbonate film, a triacetic acid cellulose film, or polyester film is mentioned. Protective films, such as polyvinyl alcohol, polyethylene terephthalate, polyolefine, polyvinyl chloride, a polyvinylidene chloride, or a cellophane film, can be used providing them further. It can laminate on this hologram recording medium by pasting together spreading by solution states, electrostatic adhesion, lamination using an extruder, or a film that applied a binder to this protective film beforehand as the method of formation of a protective film. Thus, when using it, inserting a hologram recording medium into two substrates, it is required that at least one side should be optically transparent.

[0046]Next, a manufacturing method of a hologram which uses photosensitive materials for holograms of this invention is explained. That is, interference exposure is carried out in an optical system for reflection type hologram photography which showed a recording medium for holograms created by the method, for example in Drawing 1. Although it is possible to make manufacture of a hologram complete by such only hologram exposure, in order to promote further a polymerization of a compound (B) which has a functional group in which an unreacted polymerization is possible only by this hologram exposure and to aim at fixing, it is also possible to perform heating or (and) full exposure processing. The hologram characteristic is

not spoiled even if it performs such processing. As a heat source for heat-treatment, although heat circle method oven or a heating roller is generally used suitably, it is not limited to this. Although there is no limitation in particular in heat-treatment temperature, in consideration of the heat resistance of a compound (B) which has a polymer (A) and one or more functional groups which can be polymerized containing the heat resistance of a used substrate, and a fluorine atom in photosensitive materials for holograms in this invention, it is necessary to choose suitable temperature conditions. Usually, it is for 40 to 150 °C.

[0047] As a light source used for full exposure, it is also possible visible light, such as a carbon arc, a high-pressure mercury-vapor lamp, a xenon lamp, a metal halide lamp, a fluorescent lamp, a tungsten lamp, etc. besides visible light laser, and (or) ultraviolet radiation, and to use an electron beam further.

[0048]

[Function] in the polymer (A) in which the photosensitive materials for holograms of this invention contain a fluorine atom, the compound (B) which has a functional group which can be polymerized, and the constituent which reaches a photopolymerization initiator system (C) and comprises a solvent (D). The polymer (A) containing a fluorine atom distributes to particle state in a solution. In the interference exposure of the high laser light source of coherent nature as shown in Drawing 1, the interference pattern according to the above mentioned formula (A) is formed into this recording medium using the recording medium for holograms produced by forming these photosensitive materials as a film on a substrate. Then, in the strong part of interference action, a radical (and acid) occurs from this photopolymerization initiator system, and the polymerization reaction of the compound (B) which has a functional group which can polymerize is induced by operation of light. On the other hand, in the low part of interference action, such a polymerization reaction is not induced but the density gradient produced by the volumetric shrinkage accompanying a polymerization reaction is formed by both parts. In order that the compounds (B) in which an unreacted polymerization is possible may gather by diffusion, density will go up to the strong part of interference action further, refractive index difference with the low part of interference action will be expanded to it, and the hologram by refractive index modulation is formed in it. Harder [which is a coat which is considering it as the using-polymer (A) of particle state feature especially in this invention, and is formed from the polymer of particle state]. Compared with the usual high polymer binder of solvent solubility, the diffusion in the coat of the compound (B) which carries out the functional group which can polymerize becomes easy, and said effect is imagined to have become remarkable. Although the reason is not in **, the comparatively small domain of the density formed by a particle comrade's weld is imagined to be a thing used as the course for polymerization diffusion of the compound (B) which has a functional group which can polymerize.

[0049] By choosing positively the combination from which the refractive index of the polymer

(A) and the compound (B) which has a functional group which can be polymerized which are used in this invention differs on the other hand, it becomes possible to raise the refractive-

index-modulation effect furthermore, and the effect is interpreted as having become remarkable at the time of the combination which shows the degree of refractive index

modulation of 0.005 or more. Only in combination with the compound (B) which has a functional group which such combination polymerizes [a polymer (A) and], it can realize, also when the compound (B) which has a functional group which can polymerize two or more kinds from which a refractive index differs mutually is combined, and the effect becomes still more remarkable when a difference has mutually in reactivity a compound (B) which has the

functional group which was used in that case, and which can be polymerized. Namely, such composition, (1) A fluorine atom. The combination (2) fluorine atom of the polymer and (1)

which it has. The combination (3) fluorine atom of the polymer and (ii) which it has. A

combination (6) fluorine atom with the arbitrary mixtures of the compound chosen from the

polymer, (i), or (iv) which has a combination (5) fluorine atom of the polymer and (iv) which

have a combination (4) fluorine atom of the polymer and (iii) which it has. the combination of

the polymer which it has, the compound chosen from (i) or (ii), the polymer which has the

combination (7) fluorine atom, (vi), the compound chosen from (iii) or (v), and (v) -- here, (i)

Or the inside of the compound which has an ethylenic unsaturation group which (v) can (i)

polymerize. The inside of the compound which has the ethylenic unsaturation group and sulfur

atom in which a non halogen system aliphatic compound (ii) polymerization is possible. Non

halogen system inside of the compound which has an ethylenic unsaturation group which has

an aromatic ring or (and) a halogen atom in intramolecular among the compounds which have

an ethylenic unsaturation group in which an aliphatic compound (iii) polymerization is possible,

and in which a compound (iv) polymerization is possible. The inside of the compound which

has an oxirane ring which has a sulfur atom and an aromatic ring, or (and) a halogen atom in

intramolecular, and in which a compound (v) polymerization is possible, it is a compound

which has an aromatic ring or (and) a halogen atom in intramolecular among the compounds

which have an oxirane ring in which a non halogen system aliphatic series system compound

(vi) polymerization is possible.

[0050]

Based on an example, this invention is explained more to details below, in each

following example, especially, a part expresses a weight section, as long as there is no notice.

[Manufacture of the particle dispersion liquid (A) of the polymer containing example

of manufacture 1 fluorine atom Heptane 102 Part N-butyl acetate 8 part Lumiflon LF200 (60-%

of the weight xylene solution) 108 Teach a part into a flask and heating flowing back is carried

out, A following monomer and polymerization initiator were dropped over 3 hours, and 26

copies of n-butyl acetate was added after 2 more hour aging.

Styrene 15 Part Methyl methacrylate 40 Part Acrylonitrile 30 part 2-hydroxyethyl methacrylate 15 Part Tert-butyl peroxy-2-ethylhexanoate The nonvolatile matter of the obtained dispersion liquid (A) 1.5 copies 48%, It was 0.15 micrometer in particle diameter of a polymer. [0052] Manufacture of the particle state dispersion liquid (B) of the polymer containing example of manufacture 2 fluorine atom Heptane 102 Part N-butyl acetate 8 part Lumiflon LF200 (60-% of the weight xylene solution) 108 Teach a part into a flask and heating flowing back is carried out. A following monomer and polymerization initiator were dropped over 3 hours, and 26 copies of n-butyl acetate was added after 2 more hour aging.

Styrene 15 Part The methyl methacrylate 40. Part 2-hydroxyethyl methacrylate 15 Part Guro SHIIRU methacrylate 25 copies Methacrylic acid 5 part Tert-butyl peroxy-2-ethylhexanoate The nonvolatile matter of the dispersion liquid (A) obtained 1.5 copies was 0.12 micrometer in particle diameter of a polymer 48%.

[0053] Example of manufacture 3 fluorine atom. Manufacture of the particle state dispersion liquid (C) of the polymer to contain Lumiflon LF400 (5 or 50 % of the weight of acid value xylene solution) 200 Part Guro SHIIRU methacrylate 0.8 Part 4-tert-butylpyrocatechol 0.02 copy Dimethylamino ethanol 0.1 a part. Taught into the flask and performed heating flowing back for 5 hours, it was made to react until resin acid value was set to 0.02, and the copolymeric double bond was introduced into the dispersion stabilizer chain. It was made for above-mentioned reaction mixture 130 Part Heptane 80 Part N-butyl acetate Eight copies are taught into a flask, heating flowing back was carried out, a following monomer and

polymerization initiator were dropped over 3 hours, and 26 copies of n-butyl acetate was added after 2 more hour aging.

Styrene 15 Part Methyl methacrylate 40 Part Acrylonitrile 30 Part 2-hydroxyethyl methacrylate 15 Part Tert-butyl peroxy-2-ethylhexanoate The nonvolatile matter of the obtained dispersion liquid (A) 1.5 copies 48%, It was 0.18 micrometer in particle diameter of a polymer.

[0054] The example which hits using the particle state dispersion liquid of the polymer containing the fluorine atom obtained in the example 1 of manufacture [0055] To 100 copies of the particle state dispersion liquid (A) of the polymer containing the fluorine atom obtained in the example 1 of manufacture, 50 copies of dimethylol tricyclodecane diacrylate (DCCPDA, product made from the Kyotoisha fats and oils), 0.5 copy of keto coumarin derivative (KCD), and 2.0 copies of diphenyliodonium hexafluorophosphate (DPF) were added, and the sensitizing solution for holograms was adjusted. On a 100x125x3-mm glass plate, this sensitizing solution was applied using the applicator so that the thickness after sensitizing solution desiccation might be set to 15 micrometers, and the sensitive plate for hologram recording was created. Further, as a protective layer, this was made to stick a polyethylene terephthalate film to a photosensitive

layer, and it was laminated to it. Hologram exposure by 2 light-flux interference was performed using the optical system for reflection type hologram creation shown in this recording medium for holograms at drawing 1. As laser, the 488-nm light of Ar ion laser was used at that time. Subsequently, 1 hour was neglected in 100 ° oven, subsequently full exposure of this sensitive plate that carried out hologram exposure was carried out with Xe lamp of 500W, and fixing treatment was carried out.

[0056] The diffraction efficiency of the hologram produced by making it above was measured with the product AR1 made from Jasco Industry25C type spectrophotometer. This device can install a photograph multi-meter with a 3-mm-wide slit on the circumference with a radius [centering on a sample] of 20 cm. 0.3-mm-wide monochromatic light was entered into the sample at the angle of 45 degrees, and the diffracted light from a sample was detected. The ratio of the biggest value except regular reflection light and a value when a sample is not placed but direct incident light is received was made into diffraction efficiency. The result of the obtained hologram characteristic was collectively shown in Table 2. The degree of refractive index modulation (delta n) was computed using the following formula.

$$\Delta n = \frac{\pi \cdot d}{\lambda \cdot \tan^{-1}(\eta_{112}) \cdot \cos \theta}$$

(Here, as for lambda, irradiation wave length and eta express diffraction efficiency, d expresses thickness, and theta expresses 45 degrees.)

[0057] The result when all of DCPDA of 50 copies in example 2 Example 1 were changed into dimethylol tricyclodecane diethio acrylate (DCPDSEA) and also it was operated by the same method as Example 1 was summarized in Table 2, and was shown.

[0058] The result when DCPDA of 50 copies in example 3 Example 1 was changed into DCPDA of 25 copies and neopentyl glycol diacrylate (NPGDA, the Arataka village chemicals company make) of 25 copies and also it was operated by the same method as Example 1 was summarized in Table 2, and was shown.

[0059] DCPDA of 50 copies in example 4 Example 1 DCPDA of 25 copies, The result when it changed into 2-(2-hydroxy-1,1, - dimethyl-5-ethyl-5'-hydroxymethyl)-1,3-dioxane diacrylate (R-604, Nippon Kayaku Co., Ltd. make) of 25 copies and also was operated by the same method as Example 1 was summarized in Table 2, and was shown.

[0060] DCPDA of 50 copies in example 5 Example 1 The dicyclopentadiol oxy acrylate (DCPA, Hitachi Chemical fan krill FA-513A) of 25 copies, The result when it changed into ethyleneoxide denaturation bisphenol A diacrylate (BP-4EA, product made from the Kyoeisha fats and oils) of 25 copies and also was operated by the same method as Example 1 was summarized in Table 2, and was shown.

[0061] The result when DCPDA of 50 copies in example 6 Example 1 was changed into

DCPDA of 25 copies and phenoxy ethyl acrylate (POEA, OSAKA ORGANIC CHEMICAL INDUSTRY make: screw coat #192) of 25 copies and also it was operated by the same method as Example 1 was summarized in Table 2, and was shown.

[0062]The result when DCPDA of 50 copies in example 7 Example 1 was changed into DCPDA of 25 copies and the ethoxylation tribromophenyl acrylate (the Aratanaka village chemicals company make: NK ester 530A) of 25 copies and also it was operated by the same method as Example 1 was summarized in Table 2, and was shown.

[0063]The result when DCPDA of 50 copies in example 8 Example 1 was changed into DCPDA of 25 copies and the phenoxyethylthio acrylate (POESA) of 25 copies and also it was operated by the same method as Example 1 was summarized in Table 2, and was shown.

[0064]The result when all of DCPDA of 50 copies in example 9 Example 1 were changed into POEA and also it was operated by the same method as Example 1 was summarized in Table 2, and was shown.

[Table 1]

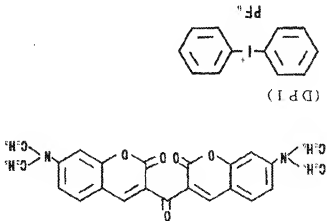
| 実施例
番号 | 重合可能な
官能基を有
する化合物
(重量部) | 連鎖移動剤
(重量部) | 増粘剤
(重量部) | 開始剤
(重量部) | 実施例 1 にて得られた化合物 | |
|-----------|----------------------------------|----------------|--------------|--------------|-----------------|------------|
| | | | | | 重合率 (%) | 重合率 (×100) |
| 1 | DCPDA (50) | なし | KCP (0.5) | DP1 (2) | なし | なし |
| 2 | DCPDA (50) | なし | KCP (0.5) | DP1 (2) | なし | なし |
| 3 | DCPDA (25)+NPDA (25) | なし | KCP (0.5) | DP1 (2) | なし | なし |
| 4 | DCPDA (25)+B604 (25) | なし | KCP (0.5) | DP1 (2) | なし | なし |
| 5 | FA513A (25)+BP-4EA (25) | なし | KCP (0.5) | DP1 (2) | なし | なし |
| 6 | DCPDA (25)+POEA (25) | なし | KCP (0.5) | DP1 (2) | なし | なし |
| 7 | DCPDA (25)+530A (25) | なし | KCP (0.5) | DP1 (2) | なし | なし |
| 8 | DCPDA (25)+POESA (25) | なし | KCP (0.5) | DP1 (2) | なし | なし |
| 9 | POEA (50) | なし | KCP (0.5) | DP1 (2) | なし | なし |

*7つの素原子を含有する高分子重合体は、製造例 1 にて得られた化合物 (48 重量部) を使用した。

[0066]

[Table 2]

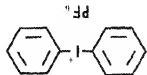
| 実施例
番号 | 照射線量
(Mrad) | 照射時間
(min) | 照射速度
(mm/min) | 照射位置
(mm) | 照射方向
(mm) | 照射角度
(°) | 照射距離
(mm) | 照射面積
(mm ²) | 照射体積
(mm ³) |
|-----------|----------------|---------------|------------------|--------------|--------------|-------------|--------------|----------------------------|----------------------------|
| 1 | 4.88 | 2.0 | 1.5 | 7.0 | 0.89 | 7.2 | 0.92 | 4.87 | 4.87 |
| 2 | 4.88 | 2.0 | 1.5 | 7.0 | 0.89 | 7.2 | 0.92 | 4.87 | 4.87 |
| 3 | 4.88 | 2.0 | 1.5 | 7.0 | 0.89 | 7.2 | 0.92 | 4.87 | 4.87 |
| 4 | 4.88 | 2.0 | 1.5 | 7.0 | 0.89 | 7.2 | 0.92 | 4.87 | 4.87 |
| 5 | 4.88 | 2.0 | 1.5 | 7.0 | 0.89 | 7.2 | 0.92 | 4.87 | 4.87 |
| 6 | 4.88 | 2.0 | 1.5 | 7.0 | 0.89 | 7.2 | 0.92 | 4.87 | 4.87 |
| 7 | 4.88 | 2.0 | 1.5 | 7.0 | 0.89 | 7.2 | 0.92 | 4.87 | 4.87 |
| 8 | 4.88 | 2.0 | 1.5 | 7.0 | 0.89 | 7.2 | 0.92 | 4.87 | 4.87 |
| 9 | 4.88 | 2.0 | 1.5 | 7.0 | 0.89 | 7.2 | 0.92 | 4.87 | 4.87 |



[0067]

[0067] [Formula 1] (KCD)

(D P 1)



[0068] The result when the sensitizing solution which was adjusted further in addition to [five copies of 2-mercapto benzoxazole (MBO)] each sensitizing solution in ten to example 18 Examples 1-9 was used as a chain transfer agent and also it was operated like Examples 1-9 was summarized in Table 4, and was shown.

[0069]

[Table 3]

| 実施例 | 重合可能な官能基を有する化合物 (重量部) | 連鎖移動剤 (重量部) | 増感剤 (重量部) | 開始剤 (重量部) |
|-----|-----------------------|-------------|-----------|-----------|
|-----|-----------------------|-------------|-----------|-----------|

| | | | | |
|-----|---------------------------|---------|-----------|---------|
| 1 0 | DCPD (50) | MBO (5) | KCD (0.5) | DP1 (2) |
| 1 1 | DCPSA (50) | MBO (5) | KCD (0.5) | DP1 (2) |
| 1 2 | DCPD (25) + MPCDA (25) | MBO (5) | KCD (0.5) | DP1 (2) |
| 1 3 | DCPD (25) + R60A (25) | MBO (5) | KCD (0.5) | DP1 (2) |
| 1 4 | FA513A (25) + BP-4EA (25) | MBO (5) | KCD (0.5) | DP1 (2) |
| 1 5 | DCPD (25) + POEA (25) | MBO (5) | KCD (0.5) | DP1 (2) |
| 1 6 | DCPD (25) + S30A (25) | MBO (5) | KCD (0.5) | DP1 (2) |
| 1 7 | DCPD (25) + POESA (25) | MBO (5) | KCD (0.5) | DP1 (2) |
| 1 8 | POEA (50) | MBO (5) | KCD (0.5) | DP1 (2) |

*7つの素原子を含む分子重合体は、製造例1にて得られた化合物 (4.8重量部) を使用した。

[0070]

[Table 4]

| 実施例 | 両剤放熱
(mJ) | 露光量
(mJ/cm ²) | 割合
(%) | 回収効率
(%) | 屈折率
(×100) | 714nmの波長
(nm) |
|-----|--------------|------------------------------|-----------|-------------|---------------|------------------|
| 10 | 4.88 | 3.0 | 1.6 | 7.3 | 0.87 | 4.88 |
| 11 | 4.88 | 4.0 | 1.6 | 7.5 | 0.90 | 4.88 |
| 12 | 4.88 | 3.0 | 1.6 | 6.8 | 0.80 | 4.90 |
| 13 | 4.88 | 3.0 | 1.6 | 7.5 | 0.90 | 4.90 |
| 14 | 4.88 | 3.5 | 1.6 | 8.7 | 1.15 | 4.88 |
| 15 | 4.88 | 3.5 | 1.6 | 9.2 | 1.33 | 4.88 |
| 16 | 4.88 | 4.0 | 1.6 | 8.0 | 0.98 | 4.92 |
| 17 | 4.88 | 3.5 | 1.6 | 7.3 | 0.87 | 4.91 |
| 18 | 4.88 | 4.5 | 1.6 | 8.0 | 0.98 | 4.92 |

[00071] Changed DCPDA of 50 copies in example 19 Example 1 into BP-4EA of 25 copies, and 3,4-epoxycyclohexylmethyl 3,4-epoxy cyclohexene carboxylate (ERL4221, made in Union Carbide) of 25 copies, and also. The result when it was operated by the same method as Example 1 was summarized in Table 6, and was shown.

[00072] The result when DCPDA of 50 copies in example 20 Example 1 was changed into DCPA of 25 copies and bisphenol F diglycidyl ether (Epicat 807, oil recovery shell epoxy company make) of 25 copies and also it was operated by the same method as Example 1 was summarized in Table 6, and was shown.

[00073] The result when DCPDA of 50 copies in example 21 Example 1 was changed into DCPDA of 25 copies and p-bromo phenyl glycidyl ether (PGE-Br) of 25 copies and also it was operated by the same method as Example 1 was summarized in Table 6, and was shown.

[00074] The result when DCPDA of 50 copies in example 22 Example 1 was changed into phenoxyethylene vinyl ether (POVE) and also it was operated by the same method as Example 1 was shown in Table 6.

[00075]
[Table 5]

| 実施例 | 重合可能な官能基を有する化合物 (重量部) | 連鎖移動剤 (重量部) | 増粘剤 (重量部) | 開始剤 (重量部) | *7、素原子を含有する高分子重合体1は、製造例1にて得られた化合物 (48重量部) を使用した。 | | | |
|-----|-----------------------|-------------|-----------|-----------|--|-------------------------|-----------|-----------------------|
| | | | | | BP-4EA (25)+ERL4221 (25) | BP-4EA (25)+PGE-Br (25) | POVE (25) | DCPA (25)+PGE-Br (25) |
| 1 9 | なし | KCD (0.5) | KCD (0.5) | BP1 (2) | なし | なし | なし | なし |
| 2 0 | なし | KCD (0.5) | KCD (0.5) | BP1 (2) | なし | なし | なし | なし |
| 2 1 | なし | KCD (0.5) | KCD (0.5) | BP1 (2) | なし | なし | なし | なし |
| 2 2 | なし | KCD (0.5) | KCD (0.5) | BP1 (2) | なし | なし | なし | なし |

[00076]
[Table 6]

| 実施例 | 照射光源 | 露光量 (mJ/cm ²) | 膜厚 (nm) | 回折効率 (%) | 配向率 (×100) | 配向率変動率 (%) |
|-----|------|---------------------------|---------|----------|------------|------------|
| 19 | 488 | 30 | 15 | 81 | 1.23 | 48.7 |
| 20 | 488 | 35 | 15 | 60 | 0.76 | 48.7 |
| 21 | 488 | 25 | 15 | 68 | 0.86 | 48.8 |
| 22 | 488 | 40 | 15 | 77 | 1.00 | 48.8 |

[0077] The result when changed KCD of 0.5 copy in example 23 Example 10 into trisbipyridine ruthenium hexafluorophosphate (Ru complex) of 1.0 copy, and the 441-nm light of helium-Cd laser was used for the light source and also it was operated by the same method as Example 10 was summarized in Table 8, and was shown.

[0078] The result when KCD of 0.5 copy in example 24 Example 10 was changed into the thioxanthene derivative (TXD) of 0.5 copy and also it was operated by the same method as Example 10 was summarized in Table 8, and was shown. [0079] The result when KCD of 0.5 copy in example 25 Example 1 was changed into the mercocyanine derivative (MCD) of 0.3 copy and also it was operated by the same method as Example 10 was summarized in Table 8, and was shown.

[0080] The result when KCD of 0.5 copy in example 26 Example 10 was changed into the unsaturation ketone derivative (DEAW) of 0.5 copy and also it was operated by the same method as Example 10 was summarized in Table 8, and was shown. [0081] The result when

changed KCD of 0.5 copy in example 27 Example 10 into the phthalocyanine derivative (PCD) of 0.2 copy, and the 676-nm light of Kr ion laser was used for the light source and also it was operated by the same method as Example 10 was summarized in Table 8, and was shown. [0082] About KCD of 0.5 copy in example 28 Example 10, it is a tetra benzoporphyrin derivative (the result when changed into TBPD, and the 633-nm light of helium-Ne laser was used for the light source and also it was operated by the same method as Example 10 was summarized in Table 8, and was shown.) of 0.2 copy.

[0083] The result when changed KCD of 0.5 copy in example 29 Example 10 into the tetrapyrano porphyrine derivative (TPZD) of 0.5 copy, and the 633-nm light of helium-Ne laser was used for the light source and also it was operated by the same method as Example 10 was summarized in Table 8, and was shown.

[0084] [Table 7]

[0086]
[Formula 2]

| 実施例 | 照射波長 (nm) | 露光量 (mJ/cm ²) | 膜厚 (μm) | 回折効率 (%) | 屈折率変動率 (×100) | 714nm波長での透過率 (nm) |
|-----|-----------|---------------------------|---------|----------|---------------|-------------------|
| 23 | 441 | 30 | 16 | 67 | 0.72 | 44.0 |
| 24 | 468 | 45 | 16 | 70 | 0.83 | 46.7 |
| 25 | 468 | 50 | 16 | 66 | 0.78 | 46.7 |
| 26 | 468 | 36 | 16 | 72 | 0.86 | 48.7 |
| 27 | 476 | 30 | 16 | 77 | 1.30 | 67.6 |
| 28 | 633 | 10 | 16 | 75 | 1.17 | 63.3 |
| 29 | 633 | 35 | 16 | 72 | 1.11 | 63.3 |

[0085]
[Table 8]

| 実施例 | | 重合可能な官能基を有する化合物 (重量部) | | 連鎖移動剤 (重量部) | | 増感剤 (重量部) | | 開始剤 (重量部) | |
|-----|------------|-----------------------|------------|-------------|--|-----------|--|-----------|--|
| 23 | DCPDA (50) | MBO (5) | 架橋体 (1.0) | DP1 (2) | | | | | |
| 24 | DCPDA (50) | MBO (5) | TXD (0.5) | DP1 (2) | | | | | |
| 25 | DCPDA (50) | MBO (5) | MCD (0.3) | DP1 (2) | | | | | |
| 26 | DCPDA (50) | MBO (5) | DEA (0.5) | DP1 (2) | | | | | |
| 27 | DCPDA (50) | MBO (5) | Pd (0.2) | DP1 (2) | | | | | |
| 28 | DCPDA (50) | MBO (5) | TBP (0.2) | DP1 (2) | | | | | |
| 29 | DCPDA (50) | MBO (5) | TP2D (0.5) | DP1 (2) | | | | | |

*7つの炭素子を含む二硫分子重合体は、製造例1にて得られた化合物 (4.8重量部) を使用した。

[0090]The result when DPl of two copies in example 32 Example 10 was changed into N-phenylglycine (NPG) of two copies and also the same operation as Example 10 was carried out was summarized in Table 10, and was shown.

[0091]The result when DPl of two copies in example 33 Example 10 was changed into the iron arene complex (IRGACURE 261:IRG261) of two copies and also the same operation as Example 10 was carried out was summarized in Table 10, and was shown.

[0092]The result when DPl of two copies in example 34 Example 10 was changed into the dimethyphenacyl SURUHONIMUTORIFENIRUBUCHIRU borate (DMPSB) of two copies and also the same operation as Example 10 was carried out was summarized in Table 10, and was shown.

[0093]The result when DPl of two copies in example 35 Example 10 was changed into the tetrabutylammonium triphenylbutyl borate (TBAB) of two copies and also the same operation as Example 10 was carried out was summarized in Table 10, and was shown.

[0094]The result when DPl of two copies in example 36 Example 10 was changed into the diphenylphenacyl sulonium TORIFENIRUBUCHIRUBORETO (DPPSB) of two copies and also the same operation as Example 10 was carried out was summarized in Table 10, and was shown.

[0095]The result when DPl of two copies in example 37 Example 10 was changed into the iron arene triphenylbutyl borate (FAB) of two copies and also the same operation as Example 10 was carried out was summarized in Table 10, and was shown.

[0096]The result when DPl of two copies in example 38 Example 10 was changed into the diphenylbiodonium triphenylbutyl borate (DPiB) of two copies and also the same operation as Example 10 was carried out was summarized in Table 10, and was shown.

[Table 9]
[0097]

重合可能な
官能基を有
する化合物
(重量部)
遷移金属剤
(重量部)
増粘剤
(重量部)
開始剤
(重量部)

| | | | | |
|-----|------------|---------|------------|------------|
| 3 0 | DCPDA (50) | MB0 (5) | KCD (0. 5) | BTB (2) |
| 3 1 | DCPDA (50) | MB0 (5) | KCD (0. 5) | TCT (2) |
| 3 2 | DCPDA (50) | MB0 (5) | KCD (0. 5) | NPG (2) |
| 3 3 | DCPDA (50) | MB0 (5) | KCD (0. 5) | IRG261 (2) |
| 3 4 | DCPDA (50) | MB0 (5) | KCD (0. 5) | DMPSB (2) |
| 3 5 | DCPDA (50) | MB0 (5) | KCD (0. 5) | TBAB (2) |
| 3 6 | DCPDA (50) | MB0 (5) | KCD (0. 5) | DPPSB (2) |
| 3 7 | DCPDA (50) | MB0 (5) | KCD (0. 5) | FAB (2) |
| 3 8 | DCPDA (50) | MB0 (5) | KCD (0. 5) | DPiB (2) |

*7、8 炭原子を含有する高分子重合体は、製造例 1 にて得られた化合物 (4 8 重量部) を使用した。

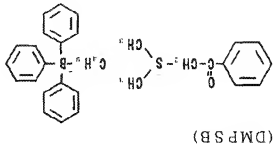
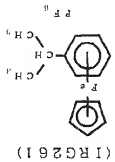
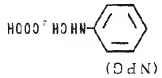
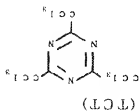
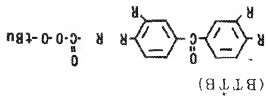
[0098]

[Table 10]

| 実施例 | 照射波長
(nm) | 露光量
(mJ/cm ²) | 膜厚
(nm) | 回折効率
(%) | 屈折率差
(×100) | 740nm 波長
(nm) |
|-----|--------------|------------------------------|------------|-------------|----------------|------------------|
| 30 | 488 | 3.0 | 1.6 | 7.3 | 0.87 | 48.7 |
| 31 | 488 | 3.0 | 1.6 | 7.3 | 0.87 | 48.7 |
| 32 | 488 | 5.0 | 1.6 | 7.0 | 0.83 | 48.7 |
| 33 | 488 | 3.0 | 1.6 | 7.2 | 0.86 | 48.7 |
| 34 | 488 | 2.5 | 1.6 | 7.5 | 0.90 | 48.7 |
| 35 | 488 | 3.5 | 1.6 | 7.3 | 0.87 | 48.7 |
| 36 | 488 | 2.5 | 1.6 | 7.2 | 0.86 | 48.7 |
| 37 | 488 | 2.5 | 1.6 | 7.5 | 0.90 | 48.7 |
| 38 | 488 | 1.5 | 1.6 | 7.3 | 0.87 | 48.7 |

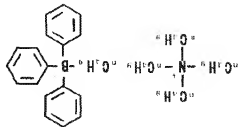
[0099]

[Formula 4]

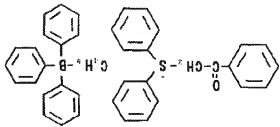


[0100]
[Formula 5]

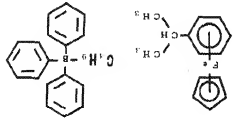
(TBA B)



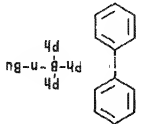
(DPPSB)



(FeAB)



(DPIB)



[0101]The result when KCD of 0.5 copy in example 39 Example 34 was changed into the cyanine derivative (CyD) of 0.3 copy and also the same operation as Example 34 was carried out was summarized in Table 12, and was shown.

[0102]The result when KCD of 0.5 copy in example 40 Example 34 was changed into the styryl derivative (StyD) of 0.3 copy and also the same operation as Example 34 was carried out was summarized in Table 12, and was shown.

[0103]The result when KCD of 0.5 copy in example 41 Example 34 was changed into the

pyriliuM derivative (PyD) of 0.5 copy and also the same operation as Example 34 was carried out was summarized in Table 12, and was shown.

[0104]The result when KCD of 0.5 copy in example 42 Example 34 was changed into the thia pyriliuM derivative (TPyD) of 0.3 copy and also the same operation as Example 34 was carried out was summarized in Table 12, and was shown.

[0105]The result when changed KCD of 0.5 copy in example 43 Example 34 into the SULKW/ARIRIUMU derivative (SqD) of 0.3 copy, the 633-nm light of helium-Ne laser was used for the light source and also it was operated by the same method as Example 34 was summarized in Table 12, and was shown.

[0106]The result when changed KCD of 0.5 copy in example 44 Example 34 into the AZURENIMU derivative (AZD) of 0.4 copy, and the 633-nm light of helium-Ne laser was used for the light source and also it was operated by the same method as Example 34 was summarized in Table 12, and was shown.

[0107]The result when changed the photopolymerization initiator system in example 45 Example 34 into the eosine Y organicity iodonium complex (EY-DP1) of 1.5 copies, and the 514-nm light of Ar ion laser was used for the light source and also it was operated by the same method as Example 34 was summarized in Table 12, and was shown.

[0108]The result when changed the photopolymerization initiator system in example 46 Example 34 into the AZURENIMU organicity boron complex (AZB) of 1.5 copies, and the 647-nm light of Kr ion laser was used and also it was operated by the same method as Example 34 was summarized in Table 12, and was shown.

[0109]
[Table 11]

| 実施例 | 重合可能な官能基を有する化合物 (重量部) | 連鎖移動剤 (重量部) | 増感剤 (重量部) | 開始剤 (重量部) |
|-----|-----------------------|-------------|---------------|-----------|
| 3 8 | DCPDA (50) | MBD (5) | CyD (0. 3) | DMPSB (2) |
| 4 0 | DCPDA (50) | MBD (5) | StyD (0. 3) | DMPSB (2) |
| 4 1 | DCPDA (50) | MBD (5) | PyD (0. 5) | DMPSB (2) |
| 4 2 | DCPDA (50) | MBD (5) | TPyD (0. 3) | DMPSB (2) |
| 4 3 | DCPDA (50) | MBD (5) | SqD (0. 3) | DMPSB (2) |
| 4 4 | DCPDA (50) | MBD (5) | AzD (0. 4) | DMPSB (2) |
| 4 5 | DCPDA (50) | MBD (5) | EY-DP1 (1. 5) | |
| 4 6 | DCPDA (50) | MBD (5) | AzB (1. 5) | |

*7 ヲ 素原子を含有する高分子重合体は、製造例 1 にて得られた化合物 (4 8 重量部) を使用した。

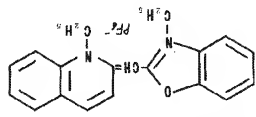
[0110]
[Table 12]

| 実施例 | 照射波長 | 露光時間 | 照射量 | 回折効率 | 回折率 | 回折率標準度 | 7°での波長 |
|------|------|-------|-----------------------|------|------|--------|--------|
| (nm) | (nm) | (sec) | (mJ/cm ²) | (%) | (%) | (%) | (nm) |
| 38 | 488 | 25 | 16 | 71 | 0.64 | 48.7 | 48.7 |
| 40 | 488 | 25 | 16 | 73 | 0.87 | 48.7 | 48.7 |
| 41 | 488 | 20 | 16 | 73 | 0.87 | 48.7 | 48.7 |
| 42 | 488 | 15 | 16 | 76 | 0.92 | 48.7 | 48.7 |
| 43 | 633 | 35 | 16 | 71 | 1.10 | 63.1 | 63.1 |
| 44 | 633 | 30 | 16 | 72 | 1.11 | 63.1 | 63.1 |
| 45 | 514 | 35 | 16 | 70 | 0.88 | 51.4 | 51.4 |
| 46 | 647 | 35 | 16 | 72 | 1.14 | 64.6 | 64.6 |

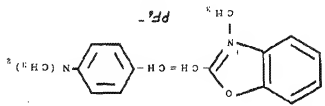
[0111]

[Formula 6]

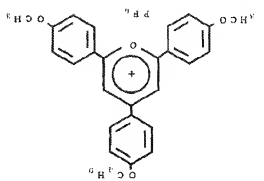
(C y D)



(S t y D)



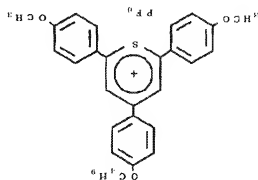
(P y D)



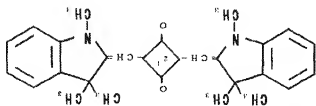
[0112]

[Formula 7]

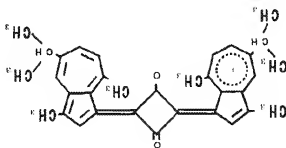
(TPyD)



(SQD)



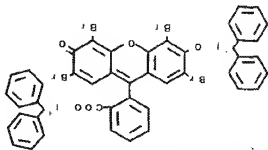
(AZD)



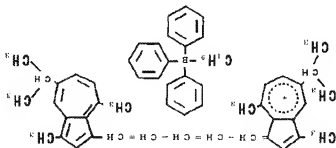
[0113]

[Formula 8]

(E Y-DP 1)



(A 2 B)



[0114] It changed into the particle state dispersion liquid of the polymer containing the fluorine atom of the example 1 of manufacture in example 47. Example 1, and 100 copies of particle state dispersion liquid of the polymer containing the fluorine atom of the example 2 of manufacture were used, and also the hologram was created by the completely same method as Example 1. The reflection type hologram in which the thickness of a film has 15 micrometers and exposure energy has the diffraction efficiency (degree of refractive index modulation = 0.0092) of 72% and the playback wavelength of 486 nm by 20 mJ/cm² was obtained.

[0115] It changed into the particle state dispersion liquid of the polymer containing the fluorine atom of the example 1 of manufacture in example 48. Example 1, and 100 copies of particle state dispersion liquid of the polymer containing the fluorine atom of the example 3 of manufacture were used, and also the hologram was created by the completely same method as Example 1. The reflection type hologram in which the thickness of a film has 17 micrometers and exposure energy has the diffraction efficiency (degree of refractive index modulation = 0.0085) of 75% and the playback wavelength of 486 nm by 22 mJ/cm² was obtained.

[0116]

[Effect of the invention] It becomes possible to manufacture the volume phase type hologram which is excellent in chemical stability or an environmental capability-proof, and has high resolution and high diffraction efficiency with little exposure energy by use of the photosensitive materials for holograms in this invention, and this recording medium.

[0117]

[Translation done.]

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(54) PHOTSENSITIVE COMPOSITION FOR VOLUME HOLOGRAM RECORDING AND
PHOTSENSITIVE MEDIUM FOR VOLUME HOLOGRAM RECORDING

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a photosensitive composition for volume hologram recording with large modulation quantity of the refractive index, for obtaining a volume hologram having controlled diffraction efficiency and half width as desired.
SOLUTION: The photosensitive composition for volume hologram recording comprises a binder resin, a photopolymerizable compound, a photoinitiator, and a sensitizer. The binder resin has 10,000 to 350,000 average molecular weight and $\geq 80^{\circ}\text{C}$ glass transition temperature. The volume hologram obtained by using the composition shows ≤ 20 nm half-value width of the diffraction spectrum and ≥ 0.03 refractive index modulation amount.

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井理士 船野 義人 |
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(5d) 【発明の名称】 体積型ホログラム記録用感光性組成物および体積型ホログラム記録用感光性媒体

(S7) 【要約】

【課題】 所望の回折効率、半値幅に制御された体積型ホログラムを得ることができる、
回折率調整量の大きい体積型ホログラム記録用感光性組成物を提供する。

【解決手段】 バイニター樹脂、光重合性化合物、光重合開始剤、および増感剤を含んでなる体積型ホログラム記録用感光性組成物であって、前記バイニター樹脂の平均分子量が1万〜3.5万で、かつ、ガラス転移温度が80℃以上であり、この組成物を用いて得られる体積型ホログラムの回折入ベクトルの半値幅が、20nm以下で、かつ、回折率調整量が0.03以上とする。

【選択図】 なし

【特許請求の範囲】

【請求項1】

パレンゾー樹脂、光重合性化合物、光重合開始剤、および増感剤を含んでなる体積型ホログラム記録用感光性組成物であって、前記パレンゾー樹脂の平均分子量が1万〜2.5万で、かつ、ガラス転移温度が80℃以上であり、この組成物を用いた感光性媒体を露光して体積型ホログラムを記録したときの、得られる体積型ホログラムの回折スベクトルの半値幅が、20nm以下で、かつ、屈折率変動量が0.03以上である、体積型ホログラム記録用感光性組成物。

【請求項2】

前記パレンゾー樹脂が、アクリル系樹脂である、請求項1に記載の体積型ホログラム記録用感光性組成物。

【請求項3】

パレンゾー樹脂、光重合性化合物、光重合開始剤、および増感剤を含んでなる体積型ホログラム記録用感光性組成物であって、

前記パレンゾー樹脂の平均分子量が3.0万〜1.0万で、かつ、ガラス転移温度が60℃以下であり、

この組成物を用いた感光性媒体を露光して体積型ホログラムを記録したときの、得られる体積型ホログラムの回折スベクトルの半値幅が、20nm以下で、かつ、屈折率変動量が0.03以上である、体積型ホログラム記録用感光性組成物。

【請求項4】

前記パレンゾー樹脂が、酢酸に二ル系樹脂である、請求項3に記載の体積型ホログラム記録用感光性組成物。

【請求項5】

パレンゾー樹脂、光重合性化合物、光重合開始剤、および増感剤を含んでなる体積型ホログラム記録用感光性組成物であって、

前記パレンゾー樹脂の平均分子量が1万〜2.6万で、かつ、ガラス転移温度が60℃以下であり、

この組成物を用いた感光性媒体を露光して体積型ホログラムを記録したときの、得られる体積型ホログラムの回折スベクトルの半値幅が、25nm以上で、かつ、屈折率変動量が0.03以上である、体積型ホログラム記録用感光性組成物。

【請求項6】

前記パレンゾー樹脂が、酢酸に二ル系樹脂である、請求項5に記載の体積型ホログラム記録用感光性組成物。

【請求項7】

請求項1〜4のいずれか1項に記載の体積型ホログラム記録用感光性組成物からなる感光層が、透明基材上に設けられてなる体積型ホログラム記録用感光性媒体であって、

体積型ホログラムを記録したときの、得られる体積型ホログラムの回折スベクトルの半値幅が、20nm以下で、かつ、屈折率変動量が0.03以上である、体積型ホログラム記録用感光性媒体。

【請求項8】

請求項5または6に記載の体積型ホログラム記録用感光性組成物からなる感光層が、透明基材上に設けられてなる体積型ホログラム記録用感光性媒体であって、

体積型ホログラムを記録したときの、得られる体積型ホログラムの回折スベクトルの半値幅が、25nm以上で、かつ、屈折率変動量が0.03以上である、体積型ホログラム記録用感光性媒体。

【請求項9】

請求項7に記載の体積型ホログラム記録用感光性媒体を用いた体積型ホログラムであって、回折スベクトルの半値幅が、20nm以下で、かつ、屈折率変動量が0.03以上である、体積型ホログラム。

【請求項10】 請求項8に記載の体積型ホログラム記録用感光性媒体を用いた体積型ホログラムであつて、回折スレートの半幅が、2.5mm以下で、かつ、屈折率変調量が0.03以上である、体積型ホログラム。

【発明の詳細な説明】

【技術分野】
体積型ホログラム用材料に関し、特に、屈折率変調(Δn)が大きく、所望の回折効率、半幅に制御された体積型ホログラムを得るための体積型ホログラム記録用感光性媒体に関する。

【背景技術】
体積型ホログラムは、物体を三次元で表現でき、高い回折効率、波長選択性を持つことと用途として幅広く利用されている。かかる体積型ホログラムは可干渉性(可干渉性)が強く、波長が等しい物体光と参照光とを干渉させて、体積型ホログラム記録用材料に入射し、物体に関する三次元情報を材料内部に干渉縞として記録することにより作製されるものである。

【0003】
この干渉縞は干渉光の明暗部分に対応した屈折率変調として記録される。また、体積型ホログラムの一つの特徴として、優れた波長選択性を有することが挙げられ、特定波長の光源(入射光)に対して、特定の角度ないし波長のみを回折し再生できる。

【0004】
近年、このような体積型ホログラムの特徴を利用して、体積型ホログラムを光学素子やフラット等分野に応用する試みが行われている。すなわち、再生回折光の中心が与えられている。

【0005】
再生光の波長や半幅を制御する方法として、例えば、特開平06-004015号公報に記載されているように光重合性化合物や可塑剤等を含有した溶液にホログラム層を浸漬し、ホログラム再生波長を変化させることが開示されている(特許文献1)。また、特開平06-004015号公報や特開平09-506441号公報には、光重合性化合物、可塑剤等からなる樹脂層をホログラム層に貼り合わせることで、ホログラム再生波長を変化させ、広帯域化することが開示されている(特許文献2および特許文献3)。

【0006】
しかしながら、光重合性化合物、可塑剤等を含有した溶液にホログラム層を浸漬する方法においては、溶液を使用する湿式法であるため、湿式処理が煩雑で製造コストがかかるため広範囲には向きである。一方、光重合性化合物、可塑剤等からなる樹脂層をホログラム層に貼り合わせる方法においては、乾式法により作製されるもの、ホログラム記録層とは別に波長制御を目的としたカラーチューニング層を設ける必要があるため、製造工程や材料等の観点から問題がある。

【0007】
【特許文献1】特開平06-4015号公報
【特許文献2】特許第2602345号公報
【特許文献3】特表平09-506441号公報

【発明の概要】
本発明者は今般、パインターとして用いる樹脂のガラス転移温度および分子量を調整することで、所望の回折効率および半幅を有する体積型ホログラムが得られるとの知見を得た。本発明はかかる知見によるものである。

【0008】

すなわち、本発明の目的は、所望の回折効率、半値幅に制御された体積型ホログラムであって、屈折率変動量の大きい体積型ホログラムを得ることができる、体積型ホログラム記録用感光性組成物および体積型ホログラム記録用感光性媒体を提供することにある。

【6000】

本発明の体積型ホログラム記録用感光性組成物は、バインダー樹脂、光重合性化合物、光重合開始剤、および増感剤を含んでなる体積型ホログラム記録用感光性組成物であって

前記パルミチン酸の平均分子量が1万〜2.5万で、かつ、溶融転移温度が80℃以上であり、この組成物を用いた発光性媒体を露光して体積型ホログラムを記録したときの得られる体積型ホログラムの回折入射角の半値幅が、2.0 m以下で、かつ、屈折率減衰率が0.03以上である。また、上記のパルミチン酸脂は、アクリル系樹脂であることが好ましい。

° 1 1 7 非 劫 摩 2

本説明の別の図表として、体積型ポログラムの体積型組成物は、ポログラムの樹脂、光重合性化合物、光重合開始剤、および増粘剤を含んでなる体積型ポログラムの記録用透光性組成物であり、前記ポログラムの平均粒径が30万〜100万であり、かつ、ポログラムの体積型ポログラムの回折スポットの半幅が、20μm以下であり、屈折率変動量が0.3以上である。また、上記のポログラムの樹脂は、樹脂と二硫化炭素とであることが好ましい。

[illegible]

【2100】

このような感状性組織物を用いることによって、所望の回折効率、半高幅で制御された体積型クログラムであって、回折率変動の大きい体積型クログラムを得ることができる。

本発明の体積型ロタラム記録用感光性組成物は、ロタラム記録用感光性組成物を用いた装置で、ロタラム記録用感光性媒体について与えらるる露光を説明する。

[0014]

【 1 0 1 5 】
本発明により提供される樹脂型ブロックポリマー記録用感光性組成物は、 β -ベンゾグリン酸、光阻剤、光阻硬化剤、および、面記録開始剤の可相しうな光長に対して有感度を有する樹脂を用いることによって、所望の回折効率および非線形の回折入射角を得ることができるとある。

例えば、回折効率が高く入ペクトルの半値幅の小さいプロファイルを有する体積型ホロ

ガラスは、光學用の記録材として有用である。一方、平皿幅が大きいプロファイルを有する積層型ホログラムでは、ホログラム像が明るく、プロファイルがフラット等により有用である。

【9100】

このように、本発明においては、使用するバインダー樹脂の材料特性を制御することにより、所望の回折入射角プロファイルを得ることを見出したものである。

【 0 0 1 7 】

以下、本発明の体積型ホログラム記録用感光性組成物を構成する各成分について説明す

【 0 0 1 8 】

(1) $\Delta \sim \Delta$ — $\Delta \sim \Delta$

本発明の体積型ホログラム記録用感光性組成物を構成するバイン樹脂は、第一の態様として、平均分子量が1万〜2.5万で、かつ、ガラス転移温度が80℃以上である。好

である。このような特性を有するパインゲル樹脂としては、アクリル系樹脂が好ましく、特に、求リ（メタ）アクリル酸エステルまたはその部分加水分解物が好適に用いられる。

【 6 1 0 0 】

また、本発明の第2の態様としてのバオスタ一樹脂は、平均分子量が30万~100万

として、かつ、相変移温度が60℃以下である。このような特性を有するポリシタレン樹脂としては、酢酸でニル系樹脂が好ましく、特に、ホリ酢酸でニル又はその加水分解物が好

 $^{\circ}\text{C}$ 에 대한 그래프를 그린다.

[0 2 0 0]

上記のような特性を有するハフター樹脂を主成分とする硬質型ホログラム記録用感光性組成物を、上記の硬質型ホログラム記録用感光性組成物を主成分とする軟質型ホログラム記録用感光性組成物を用いた硬質型ホログラムにおいて、回折入ベクトルの半値幅が、 20 nm 以下

施設に適用である。すなわち、回折効率が高く、かつ半価幅が小さく波長選択性に優れた20

への応用に好適である。

【 0 0 2 1 】

また、本発明の第三の態様として、バイオスター樹脂の平均分子量が1万〜2.6万で、か

5、シウ入転移温度が60℃以下である。好ましい態様としては、平均分子量が1万~25万で、かつ、シウ入転移温度が60℃以上である。このような特性を有するポリマー

酸として、酢酸で三ルオキシドが好ましく、特に、ホリ酢酸で三ル又はその加水分解物が好適に用いられる。

【2200】

上記のような高粘特性を有するハイソクノ樹脂を用いては、回折スベクトルの半値幅が、2.5 nm

以上で、かつ、好塩性菌類あり、0.3以上であり、フラスコアッシャー等での明るさ計を要
 求される分野に好適に用いることができる。すなわち、半鎖糖が大きく、かつ広範囲の液

その元を有効に利用して、團隊が明るくなるため、
 がより高く要求される分野への応用に好適である。

【0023】

なお、本発明に用いる「平均分子量」なる用語は、重量平均分子量を意味し、ゲル濾過法(GPC)により測定し、ポリアチレン換算した値である。また、ガラス転移温度は、

一、發汗、動筋結果時測定、示差熱分析、ないし公知の手段により測定できるが、本発明に於いては、動筋結果時測定における損失正接が最大値をとる温度を当該筋肉のガラス転移

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開発したものである。さらに、風折率変動量（以下、 Δn としよう）は、Kogelnikの下
記離散式 (Bell Syst. Tech. J., 48, 2909 (1969) に記載) より算出されるものである。

$$(\theta \text{ s o c } \gamma / p (u \nabla) x) _ z \text{ u e t } = k$$

(2.2.2) η は回折効率、 p は感材膜厚、 λ は記録光の波長

の媒材中への入射角度である。)

本発明においては、上記のバリエーション一機體に限定されるのではなく、所定の特性値を具する機體を用いることができるというまでもない。具体的には、求りに二アルコ

ルまたはその部分ノせヨ一ル比喩、ナリイセサル日入、来リイテクツシ、来リク
キエノ、来リク口口口口、今一口口、来リ又チシ、来リニルマナル、

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ポリクロロエチレン、ポリ塩化ビニル、ポリアクリレート、塩素化ポリエチレン、塩素化ポリプロピレン、ポリビニルアルコール又はその誘導体、ポリ-N-エチルピロリドン又はその誘導体、ポリアクリレート、メチレンと無水マレイン酸の共重合体またはそのホモポリマー、ポリビニルアルコール、メタクリル酸、メタクリル酸エステル、酢酸ビニル等の共重合可能なモノマー一群の少なくとも1つを重合成分とする共重合体等、またはそれらの混合物が用いられる。さらに、共重合成分として、熱硬化または光硬化可能な硬化性官能基を含有するモノマーを使用することができ、このように硬化性モノマーを用いることにより、膜強度が向上し、耐熱性や機械強度が向上する。

【0024】

また、パルメチン酸として、オリゴマー化の硬化性樹脂を使用することもでき、例えば、ビスフエノールA、ビスフエノールS、ノボラック、オレフィンノボラック、および、p-アルキルフェノールノボラック等の各種フェノール化合物と、エタクロロエチレンとの縮合反応により生成されるエポキシ化合物等が挙げられる。

【0025】

さらに、パルメチン酸として、アルキル反応を利用した有機-無機ハイブリッド樹脂を使用することもできる。有機-無機ハイブリッドポリマーとしては、例えば、下記一般式(1)で表わされる、重合性基を有する有機金属化合物とビニルモノマーの共重合体が挙げられる。

$$R_m M (OR)^n \quad (1)$$

(ここで、MはSi、Ti、Zr、Zn、In、Sn、Al、またはS等の金属であり、Rは炭素数1〜10のビニル基、または(メタ)アリール基であり、R'は炭素数1〜10のアルキル基であり、m+nは金属Mの価数を表す。)

シラン、ビニルトリメチシラン、ビニルトリブチシラン、ビニルトリブチルエーテル、ビニルトリブチルエーテル、および、メタクリロイルトリメチシラン等が挙げられるが、これらに限定されるものではない。

【0026】

また、ビニルモノマーとしては、例えば、アクリル酸、アクリル酸エステル、メタクリル酸、およびメタクリル酸エステルが挙げられるが、これらに限定されるものではない。

【0027】

さらに、パルメチン酸と光重合性化合物との屈折率差を大きくするために、下記一般式(2)で表わされる、有機金属化合物を組成物中に添加することもできる。

$$M' (OR)^n \quad (2)$$

(ここで、M'はTi、Zr、In、Sn、Al、またはS等の金属であり、R'は炭素数1〜10のアルキル基であり、n'は金属M'の価数を表す。)

により、上記のパルメチン酸と銅イオンを形成するため、パルメチン酸の屈折率を上げるだけなく、ホログラム記録媒体とした時の膜の強靱性や耐熱性を向上させることもできる。光重合性化合物との屈折率差を上げるためには、できるだけ屈折率の高い金属(M')を有する有機金属化合物化を用いることが好ましい。

【0028】

(2) 光重合性化合物

本発明の有機型ホログラム記録用感光性組成物を構成する光重合性化合物としては、光ラジカル重合性化合物、光カチオン重合性化合物、ないし光二量性化合物等が挙げられる。これら光重合性化合物の含有量としては、パルメチン酸100重量部に対して10〜1000重量部、好ましくは10〜200重量部である。

【0029】

二重結合を持つ化合物が挙げられ、例えば不飽和カルボニル酸、及びその塩、不飽和カルボ

記日協とあり、下相日協が手けられ、奥味附として、蘭蘭旗多圖りあり、元記日協と平座

— 1137 —

[illegible][illegible]

$\frac{1}{\sqrt{2}} \begin{pmatrix} 1 & i \\ 0 & 1 \end{pmatrix}$

1) $\forall x \in \mathbb{R} \exists y \in \mathbb{R} (x + y = 0)$ 2) $\exists x \in \mathbb{R} \forall y \in \mathbb{R} (x + y = 0)$ 3) $\forall x \in \mathbb{R} \forall y \in \mathbb{R} (x + y = 0)$ 4) $\exists x \in \mathbb{R} \exists y \in \mathbb{R} (x + y = 0)$

2-7E / #I J K L M N O P Q R S T U V W X Y Z - 2 , 1-7E / #I J K L M N O P Q R S T U V W X Y Z - 2

[illegible]
$$7x - 12y + 11z = 1 \quad 9 - 12z = 1 \quad 9 - 12z = 1 \quad 9 - 12z = 1$$

ル) フルオレン、9, 9-ビズ(4-アクリロキシジプロポキシフェニル)フルオレン、

ルズ(4-アクリロキシエトキシル-3-エチルフェニル)フルオレン、9, 9-ビス(4-

【0030】

「ニルナルホソ、4、4'、-ピアス（R-アクリロイルオキシエチルモノ）シブニルサト

ラフロモジツエニルクトン、2, 4-ピヌ (β -アクリロイルオキシエチルチオ) ジツエ

[1800]

[illegible]

また、光カチオン重合性化合物としては、エポキシ環やオキサタン環に代表される環状

環含有化合物を挙げる。ポリアルキルシクロールジグリシジルエーテル、ビスフェノール

[illegible][illegible]

金属微粒子としては屈折率が高いTi、Zr、Zn、I₂、S₂等が例示される。光重合

ルホニウム、トリア（４－メチルフェニル）スルホニウム等のスルホニウムのクロリド、
 フロミド、ホウフッ化塩、ヘキサフルオロホスフェート塩、ヘキサフルオロアセチル
 トリブシム、２－フェニル（トリクロロメチル）－１，３，５－トリアジンを、
 アジニ、２－フェニル（トリクロロメチル）－１，３，５－トリアジンを等の２，４，
 ６－置換－１，３，５－トリアジン化合物が挙げられるが、これらに限定されるものでは
 ない。

【0039】
 光重合開始剤は、記録されたホログラムの安定化の観点から、ホログラム記録後に分解
 処理されるのが好ましい。

【0040】
 (4) 増感剤

本発明の体積型ホログラム記録用感光性組成物を構成する増感剤は、上記の光重合開始
 剤の記録光に対する感度を増感せしめる役割を担うものである。具体的には、チオレリ

ウム系色素、スロシニア系色素、キノリン系色素、スチリル系色素、チオレリウム系色素、
 マリオン系色素、チオキソベンゾ系色素、キソベンゾ系色素、オキノール系色素、スロシ
 ニア系色素、ロータミ系色素、スロシニア系色素、スロシニア系色素、スロシニア系色素、スロシ

ニア系色素等が例示される。スロシニア系色素の具体例としては、
 3'－ジカルボキシエチル－2，2'－キノシニアジプロミド、1'－カルボキシエチル－
 2，2'－キノシニアジプロミド、3'－エチル－5'－[(3'－エチル－2'－(3H)－ベン

ゾチゾリリチン)エチリチン]－2'－チオキソ－4'－チオキソジプロミド等が挙げられ、
 マリオン系色素の具体例としては、3'－カルボキシエチル（7'－ジエチルメチル）－
 1'－エチルメチル（7'－ジエチルメチル）－3'，3'－カルボキシエチル（5'，7'－ジメチル

キソ）－3'，3'－カルボキシエチル（7'－ジメチル）－3'，3'－カルボキシエチル（5'，7'－ジメチル）
 等が挙げられるが、

【0041】
 これらに限定されるものではない。

可視光増感剤は、光素子のような高透明性が要求される場合には、ホログラム記録後
 の後工程や、加熱や紫外線照射時に、分解等により無色になるものが好ましい。

【0042】
 また、該増感剤の含有量は、パインダー樹脂100重量部に対して0.01～10重量
 部、好ましくは0.01～3重量部である。

【0043】
 これらの体積型ホログラム記録用感光性組成物は、溶媒に溶解させて塗布液として用い
 る。溶媒としては、アセトン、メチルエチルケトン、メチルイソブチルケトン、シクロヘ

キサノン、ベンゼン、トルエン、キシレン、クロロベンゼン、クロロホルム、メチ
 ルセルソルブ、エチルセルソルブ、メチルセルソルブ、エチルセルソルブ、エチルセル
 ソルブ、酢酸エチル、1，4-ジオキサソ、1，2-ジオキサソ、シクロヘキサノ、

クロホルム、メタノール、エタノール、イソプロパノール等、が挙げられるが、これら
 に限定されるものではない。

【0044】
 2. 体積型ホログラム記録用感光性媒体
 次に、上記の体積型ホログラム記録用組成物を用いた体積型ホログラム記録用感光性媒

【0045】
 体について説明する。

本発明における体積型ホログラム記録用感光性媒体は、上記の組成物からなる感光層を
 透明基材上に設けてなるものであり、その組成物を構成するパインダー樹脂の性質によっ
 て、露光後の体積ホログラム特性が異なるものである。

手なわら、パルマ一樹脂として、平均分子量が1万〜2.5万で、かつ、軟化温度が80℃以上のアクリル樹脂を用いた場合は、平均分子量が3万〜1.0万で、かつ、軟化温度が60℃以下の酢酸ニル系樹脂を用いた場合は、体積水口ラジエーター、度か、2.5 m以上で、かつ、屈折率調整量が0.03以上である。

依據型ホログラム記録用感光性媒体は、基材上に、上記の組成物からなる塗布液を、スピンコート、フローコート、コンフォーター、ないし、パコーター等を用いて、塗布し、乾燥し、感光層を形成することにより得られる。

【0048】
体積型水口グラム配製用感光性媒体に用いる基材としては、透明性を有する樹脂等であれば良く、ポリエチレンアクリルム、ポリプロピレンアクリルム、ポリブテンアクリルム、ポリメタクリレート系ノリ

[illegible]

路盤材の厚度としては2~2.00m、好ましくは1.0~1.50mである。上記組成物は、乾燥後の乾燥布膜に粘着性がある場合、乾燥フィルムとして上記材料として例示したフィルムを用い、該フィルムを塗布面上にミキサーすることによって得られる。乾燥布膜と塗布面との接触後は、後から剥がしやすくなる。腐蝕部がもたらすような害も良好である。

【0050】
3. 体積ホログラムの記録方法

ホログラムの記録には、可視レーザー光、例えば、アルゴンイオンレーザー（4.5 m、4.88 m、5.14、5 m）、クリプトンイオンレーザー（6.47、1 m）、ヘリウムネオンレーザー（6.3 m）、YAGレーザー（5.32 m）等のレーザー光を用いて、体積型ホログラム記録用感光性媒体に記録するとができる。

【0051】
 体験型ホログラム記録用感光性媒体に体験型ホログラムを記録する方法としては、従来から知られているいずれの方法を用いても良い。

例え、体積型ホログラム記録用感光性媒体のホログラム記録材料層に原像を密着させ、透明基材フィルム側から可視光、あるいは紫外光や電子線のような電離放射線を用いて干渉露光を行うことにより体積型ホログラムが記録される。

【0053】
また、屈折率変動の促進、重合反応完結のために、干渉露光後、紫外線による全面露光や加熱等の処理を適宜行うことができる。

【0054】
 このようにして得られた秋型型ホログラムにおいては、公知の技術を用いて、透過率パターンの測定することにより、回折入パターンの得ることができ、本発明における「半振幅」なる用語は、回折入パターンの示す波長における、回折入パターンの入射率と入射パターンの透過率との差、 $(T_1 - T_2) / 2$ の値での入射パターンの幅を意味するものである。

【0055】

実施例 1

下記に示す材料を用いて、体積型ホログラム記録用感光性組成物を調整した。

【0056】

ホリメタルメタクリレート

(ホリスチレン換算重量平均分子量：1万5千)

1, 6-ヘキソシオールシリシルエーテル

(ホリセテムメタクリラックX-212)

シエノキシエタノールメソジフクリレート

(大阪ガス製BPEFA)

ジエリールヨロニウム塩(ローチア製、P12074)

2, 5-ビス-(4-エチルブシノペンジフ)シクロペンタノ

1-ブタノール

メチルエチルケトン

上記の調整した溶液を、3.8μmのホリエチレンチレンチラフタレート(PET)フィルム(東レ製ルミラート-60)上にバキュームを使用して、乾燥膜厚10μmとなるように塗布し、体積型ホログラム記録用感光性媒体を製作した。

感光層側をミラーにラミネートし、PET側から532nmレーザー光を60mJ/cm²入射して、体積型ホログラムを記録した。

【0057】

次いで、加熱、紫外線全面照射により感光層を固定し、体積型ホログラムを得た。

得られた体積ホログラムについて、分光光度計(島津製作所製UVPC-3100)の透過率測定を行い、屈折率差調整(Δn)、回折効率、および半値幅の算出を行った。

【0058】

なお、回折効率ηは、得られた透過スベクトルのピーク透過率をT_p、ヘースライソの透過率をT_bとして、下記式、

$$\eta = (T_b - T_p) / T_p$$

により算出し、半値幅($T_{1/2}$)は、透過率のピーク値(T_p)とヘースライソ透過率(T_p)の差の1/2の値を下記式、

$$T_{1/2} = (T_p - T_b) / 2$$

により算出し、T_{1/2}時の透過スベクトル(透過波長)幅を半値幅とした。得られた、

【0059】

回折効率および半値幅の値を用いて、上記のKogelnik理論式によりΔnを算出した。

実施例 2

下記に示す材料を用いて、体積型ホログラム記録用感光性組成物を調整した。

ホリメタルメタクリレート

(ホリスチレン換算重量平均分子量：7万)

1, 6-ヘキソシオールシリシルエーテル

(ホリセテムメタクリラックX-212)

シエノキシエタノールメソジフクリレート

(大阪ガス製BPEFA)

ジエリールヨロニウム塩(ローチア製、P12074)

2, 5-ビス-(4-エチルブシノペンジフ)シクロペンタノ

1-ブタノール

メチルエチルケトン

【0060】

実施例 1と同様にして、体積型ホログラム作製し、諸物性についての測定を行った。

実施例 3

下記に示す材料を用いて、体積型ホログラム記録用感光性組成物を調整した。

ホリメタルメタクリレート

[illegible]

メチルエチルケトン
実施例 1 と同様にして、体積型ホログラム作製し、諸物性についての測定を行った。

【0064】

下記に示す材料を用いて、体積型ホログラム記録用感光性組成物溶液を調整した。

(求リ酢酸エニル
(求リスチレン換算重量平均分子量：10万)
1, 6-ヘキサメチルシクロシロエチル
70 重量部
100 重量部

(オキサセラムチックス製 EX-212)
シエノキシエタノールメチルシクロシロエチル
70 重量部
10 重量部

(大阪ガス製 B P E F A)
シアリールヨードニカム塩 (ローチイア製、P I 2074)
2, 5-エス- (4-ジエチルフェニルメチルシクロペンタノ
5 重量部
80 重量部

メチルエチルケトン
実施例 1 と同様にして、体積型ホログラム作製し、諸物性についての測定を行った。

【0065】

下記に示す材料を用いて、体積型ホログラム記録用感光性組成物溶液を調整した。

(求リ酢酸エニル
(求リスチレン換算重量平均分子量：26万)
1, 6-ヘキサメチルシクロシロエチル
100 重量部
20 重量部

(オキサセラムチックス製 EX-212)
シエノキシエタノールメチルシクロシロエチル
70 重量部
80 重量部

(大阪ガス製 B P E F A)
シアリールヨードニカム塩 (ローチイア製、P I 2074)
2, 5-エス- (4-ジエチルフェニルメチルシクロペンタノ
5 重量部
30 重量部

メチルエチルケトン
実施例 1 と同様にして、体積型ホログラム作製し、諸物性についての測定を行った。

【0066】

下記に示す材料を用いて、体積型ホログラム記録用感光性組成物溶液を調整した。

(求リ酢酸エニル
(求リスチレン換算重量平均分子量：17万)
1, 6-ヘキサメチルシクロシロエチル
100 重量部
70 重量部

(オキサセラムチックス製 EX-212)
シエノキシエタノールメチルシクロシロエチル
80 重量部
5 重量部

(大阪ガス製 B P E F A)
シアリールヨードニカム塩 (ローチイア製、P I 2074)
2, 5-エス- (4-ジエチルフェニルメチルシクロペンタノ
1 重量部
30 重量部

メチルエチルケトン
実施例 1 と同様にして、体積型ホログラム作製し、諸物性についての測定を行った。

【0067】

下記に示す材料を用いて、体積型ホログラム記録用感光性組成物溶液を調整した。

(求リスチレン換算重量平均分子量：10万)
1, 6-ヘキサメチルシクロシロエチル
100 重量部
50 重量部

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* NOTICES *

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2.*** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[Field of the Invention]

[0001]

About the charge of volume type hologram material, especially, refractive index modulation (delta n) is large and it is related with the photosensitive composition for volume type hologram record for obtaining the volume type hologram controlled by desired diffraction efficiency and half breadth, and the photosensitive medium for volume type hologram record.

[Background of the Invention]

[0002]

The volume type hologram can express an object by three dimensions, and since having high diffraction efficiency and wavelength selectivity and advanced production technology are required, it is broadly used as a design use, a security use, and an optical element use. This volume type hologram has high coherence nature (coherence), wavelength makes equal object light and reference beam interfere, and enters into volume type hologram writing materials, and it is produced by recording the three dimensional information about an object on the inside of material as an interference fringe.

[0003]

This interference fringe is recorded as refractive index modulation corresponding to the light-and-darkness portion of the interference light. It is mentioned, and to the light source (input light) of a specified wavelength, having the outstanding wavelength selectivity as one feature of a volume type hologram diffracts only the light of a specific angle thru/or wavelength, and it can be reproduced.

[0004]

In recent years, the trial which applies a volume type hologram to fields, such as an optical element and graphic arts, is made using the feature of such a volume type hologram. That is,

changing regenerated light into the light which has a specific profile is performed by controlling the center wavelength and half breadth of the reproduction diffracted light.

[0005]

As a method of controlling the wavelength and half breadth of regenerated light, a hologram layer is immersed in the solvent containing a photopolymerization nature compound, a plasticizer, etc., for example as indicated to JP,06-004015,A, and changing a hologram reproducing wave length is indicated (patent documents 1). Changing a hologram reproducing wave length and broadband-izing it is indicated by pasting together to a hologram layer the resin layer which becomes the patent No. 2602345 gazette and the Patent Publication Heisei No. 506441 [09 to] gazette from a photopolymerization nature compound, a plasticizer, etc. (the patent documents 2 and patent documents 3).

[0006]

However, in the method of immersing a hologram layer in the solvent containing a photopolymerization nature compound, a plasticizer, etc., since it is the wet process which uses a solvent, wet-developing processing is complicated, and since a manufacturing cost is applied, it is unsuitable for mass production. In the method of on the other hand pasting together to a hologram layer the resin layer which consists of a photopolymerization nature compound, a plasticizer, etc., although produced by a dry method, since it is necessary to provide the color tuning layer aiming at wavelength control apart from a hologram recording layer, there is a problem from a viewpoint of a manufacturing process, material, etc.

[Patent documents 1] JP,06-4015,A

[Patent documents 2] The patent No. 2602345 gazette

[Patent documents 3] The Patent Publication Heisei No. 506441 [09 to] gazette

[Summary of invention]

[0007]

This invention persons acquired knowledge that the volume type hologram which has desired diffraction efficiency and half breadth is obtained by adjusting the glass transition temperature and the molecular weight of the resin used as a binder this time. This invention is based on this knowledge.

[0008]

That is, the purpose of this invention is the volume type hologram controlled by desired diffraction efficiency and half breadth, and there is in providing the photosensitive composition for volume type hologram record and the photosensitive medium for volume type hologram record which can obtain a volume type hologram with the large amount of refractive index modulation.

[0009]

The photosensitive composition for volume type hologram record of this invention is a

photosensitive composition for volume type hologram record containing binder resin, a photopolymerization nature compound, a photopolymerization initiator, and a sensitizer, The average molecular weights of said binder resin are 10,000-250,000, and glass transition temperature is not less than 80 **, The half breadth of the diffraction spectrum of a volume type hologram in which it is obtained when the photosensitive medium using this constituent is exposed and a volume type hologram is recorded is 20 nm or less, and the amount of refractive index modulation is 0.03 or more. As for the above-mentioned binder resin, it is preferred that it is acrylic resin.

[0010]

The photosensitive composition for volume type hologram record as another mode of this invention, it is a photosensitive composition for volume type hologram record containing binder resin, a photopolymerization nature compound, a photopolymerization initiator, and a sensitizer, and the average molecular weights of said binder resin are 300,000-1 million, and glass transition temperature is 60 ** or less. The half breadth of the diffraction spectrum of a volume type hologram in which it is obtained when the photosensitive medium using this constituent is exposed and a volume type hologram is recorded is 20 nm or less, and the amount of refractive index modulation is 0.03 or more.

[0011]

The photosensitive composition for volume type hologram record as another mode of this invention, it is a photosensitive composition for volume type hologram record containing binder resin, a photopolymerization nature compound, a photopolymerization initiator, and a sensitizer, and the average molecular weights of said binder resin are 10,000-260,000, and glass transition temperature is 60 ** or less. The half breadth of the diffraction spectrum of a volume type hologram in which it is obtained when the photosensitive medium using this constituent is exposed and a volume type hologram is recorded is not less than 25 nm, and the amount of refractive index modulation is 0.03 or more.

As for the above-mentioned binder resin, it is preferred that it is vinyl acetate system resin.

[0012]

By using such a photosensitive composition, it is the volume type hologram controlled by desired diffraction efficiency and half breadth, and a volume type hologram with the large amount of refractive index modulation can be obtained.

[Detailed Description of the invention]

[0013]

It explains in more detail about the photosensitive medium for volume type hologram record

using the photosensitive composition for volume type hologram record and this photosensitive composition of this invention.

[0014]

1. Photosensitive composition for volume type hologram record
The photosensitive composition for volume type hologram record provided by this invention consists of binder resin, a photopolymerization nature compound, a photopolymerization initiator, and a sensitizer to which sensitization of the sensitivity to the visible-laser-beams wavelength of said photopolymerization initiator is carried out.
When the molecular weight and glass transition point use the resin which has a predetermined range as this binder resin, the volume hologram which has desired diffraction efficiency and a diffraction spectrum of half breadth can be obtained.

[0015]

For example, the volume type hologram which has a high profile with small half breadth of a spectrum has useful diffraction efficiency as a recording material for optics. In the volume type hologram which, on the other hand, has a profile with large half breadth, a hologram image is bright and useful to graphic arts etc.

[0016]

Thus, the material physical properties of the binder resin to be used are controlled by this invention.
Therefore, it finds out that the volume type hologram which has a desired diffraction-spectrum profile can be obtained.

[0017]

Hereafter, each ingredient which constitutes the photosensitive composition for volume type hologram record of this invention is explained.

[0018]

(1) Binder resin

As the first mode, average molecular weights are 10,000-250,000, and the binder resin which constitutes the photosensitive composition for volume type hologram record of this invention is not less than 80 ** in glass transition temperature. As a desirable mode, average molecular weights are 10,000-110,000, and glass transition temperature is not less than 80 **. As binder resin which has such the characteristics, acrylic resin is preferred and poly(meta) acrylic ester or its partial hydrolysate is used especially suitably.

[0019]

Average molecular weights are 300,000-1 million, and binder resin as the 2nd mode of this invention is 60 ** or less in glass transition temperature. As binder resin which has such the

characteristic, vinyl acetate system resin is preferred and polyvinyl acetate or its hydrolyzate is used especially suitably.

[0020]

In the volume type hologram using the photosensitive composition for volume type hologram record containing the binder resin which has the above physical properties, The half breadth of a diffraction spectrum is 20 nm or less, and the amount of refractive index modulation is 0.03 or more, and it can apply to an optical application as a hologram with high diffraction efficiency. That is, since diffraction efficiency excels [half breadth] in wavelength selectivity small highly, the light of a specified wavelength can be efficiently diffracted to a specific direction, and it is suitable for the application to a diffraction optical element, a wavelength selection filter, etc.

[0021]

As the third mode of this invention, the average molecular weights of binder resin are 10,000-260,000, and glass transition temperature is 60 ° or less. As a desirable mode, average molecular weights are 10,000-250,000, and glass transition temperature is not less than 60 °. As binder resin which has such the characteristic, vinyl acetate system resin is preferred and polyvinyl acetate or its hydrolyzate is used especially suitably.

[0022]

In the volume type hologram using the photosensitive composition for volume type hologram record containing the binder resin which has the above material physical properties, The half breadth of a diffraction spectrum is not less than 25 nm, and the amount of refractive index modulation is 0.03 or more, and it can use conveniently for the field as which luminosties, such as graphic arts, are required. That is, since the light of wavelength with it can be used effectively and a picture becomes bright, visibility is suitable for POP, premium goods, etc. to the application to the field demanded more highly. [large and half breadth and] [wide range]

[0023]

An "average molecular weight" [which is used for this invention] The becoming term is the value which meant average molecular weight, measured by gel filtration technique (GPC), and carried out polystyrene conversion. Generally, although glass transition temperature can be measured with dynamic viscoelasticity measurement, differential thermal analysis, or a publicly known technique, in this invention, it makes temperature to which the loss tangent in dynamic viscoelasticity measurement takes the maximum the glass transition temperature of the resin concerned. The amount of refractive index modulation (delta n is said hereafter) is computed from the following theoretical formula (it indicates to Bell Syst. Tech. J., 48, and 2909 (1969)) of Kogelnik.

$$\text{Eta}=\tanh^2\left(\pi\left(\text{delta n}\right)/\text{lambda cos theta}_0\right)$$

(Here, as for diffraction efficiency and d, a record laser wavelength and theta₀ of sensitized

material thickness and lambda are [eta] the degrees of incidence angle to the inside of the sensitized material or recording laser light.)

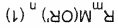
In this invention, it cannot be overemphasized that not ** limited to the above-mentioned binder resin but resin possessing a predetermined property value can be used. Specifically Polyvinyl alcohol or its partial acetalization thing, Triacetyl cellulose, polyisoprene, polybutadiene, polychloroprene, Silicone rubber, polystyrene, a polyvinyl butyral, polychloroprene, Polyvinyl chloride, polyarylate, chlorinated polyethylene, chlorinated polypropylene, Poly-N-vinylcarbazole or its derivative, Poly N-vinyl pyrrolidone, or its derivative, The copolymer or its half ester of polyarylate, styrene, and a maleic anhydride, Acrylic acid, acrylic ester, methacrylic acid, methacrylic acid ester, Those mixtures, such as acrylamide, acrylic nitril, ethylene, least one of the copolymerizable monomer groups, such as acrylamide, acrylic nitril, ethylene, propylene, VCM/PVC, and vinyl acetate, as a polymerization component, are used. The monomer containing the hardenability functional group in which heat curing or photo-curing is possible can be used as a copolymer component. Thus, by using a hardenability monomer, film strength improves and heat resistance and mechanical strength improve.

[0024]

Oligomer type hardening resin can also be used as binder resin, For example, various phenolic compounds, such as bisphenol A, the bisphenol S, novolac, o-cresolnovolac, and p-alkylphenol novolac, the epoxy compound generated by the condensation reaction with epichlorohydrin, etc. are mentioned.

[0025]

Organic-inorganic matter hybrid resin using a sol gel reaction can also be used as binder resin. As that of organic - inorganic matter hybrid polymer, the copolymer of the organic metallic compound and vinyl monomer which are expressed with a following general formula (1) and which have a polymerization nature group is mentioned, for example.



(Here, M is metal, such as Si, Ti, Zr, Zn, In, Sn, aluminum, or Se, R is a vinyl group of the carbon numbers 1-10, or (meta) an acrylyl group, R' is an alkyl group of the carbon numbers 1-10, and m+n expresses the valence of the metal M.)

As an organic metallic compound in the case of using Si as metal, For example,

vinyltriethoxysilane, vinyltrimethoxysilane, BINIRUTORI butoxysilane, Although a vinyl triary

oxysilane, a vinyltetraethoxysilane, a vinyl tetramethoxy silane,

acryloxypropyltrimethoxysilane, methacryloxy propyl trimethoxysilane, etc. are mentioned, it

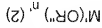
is not limited to these.

[0026]

Although acrylic acid, acrylic ester, methacrylic acid, and methacrylic acid ester are mentioned as a vinyl monomer, for example, it is not limited to these.

[0027]

In order to enlarge refractive index difference of binder resin and a photopolymerization nature compound, the organic metallic compound expressed with a following general formula (2) can also be added in a constituent.



(Here, M' is metal, such as Ti, Zr, Zn, In, Sn, aluminum, or Se, R' is an alkyl group of the carbon numbers 1-10, and n' expresses the valence of metal M').

putting under existence of water thru/or an acid catalyst, if the above-mentioned organic metallic compound is added -- sol -- by a -***** reaction, since above-mentioned binder resin and network structure are formed, it not only raises the refractive index of binder resin, but it can also raise the toughness of a film when it is considered as a hologram recording medium, and heat resistance. In order to raise refractive index difference with a photopolymerization nature compound, it is preferred to use the organic metallic compound combination which has metal with a refractive index high as much as possible (M').

[0028]

(2) Photopolymerization nature compound

As a photopolymerization nature compound which constitutes the photosensitive composition for volume type hologram record of this invention, an optical radical polymerization nature compound, an optical cationic polymerization nature compound, or an optical Ni quantification nature compound is mentioned. As content of these photopolymerization nature compound, it is ten to 200 weight section preferably ten to 1000 weight section to binder resin 100 weight section.

[0029]

The compound which has an ethylenic unsaturated double bond in which at least one addition condensation is possible as an optical radical polymerization nature compound is mentioned. For example, unsaturated carboxylic acid and its salt, ester of unsaturated carboxylic acid and an aliphatic polyalcohol compound, and the amide bond thing of unsaturated carboxylic acid and an aliphatic polyamine compound are mentioned. The monomer of ester of an aliphatic polyalcohol compound and unsaturated carboxylic acid is mentioned as an example. As acrylic ester, ethylene glycol diacrylate, triethylene glycol diacrylate, 1,3-butanediol diacrylate, tetramethylene glycol diacrylate, Propylene glycol diacrylate, neopentyl glycol diacrylate, Trimethylolpropane triacrylate, TORIMECIII roll pro panty (acryloyloxypropyl) ether, Trimethylol triacrylate, hexanediol diacrylate, 1,4-cyclohexanediol diacrylate, tetraethylene glycol diacrylate, pentaerythritol diacrylate -- and, [pentaerythritol doria] Pentaerythritol tetraacrylate, dipentaerythritol diacrylate, Dipentaerythritol triacrylate, dipentaerythritol tetraacrylate, dipentaerythritol hexaacrylate -- and, [sorbitol doria] Sorbitol tetraacrylate, sorbitol pentaacrylate, sorbitol hexa acrylate, Tori (acryloyloxyethyl) isocyanurate, polyester-

acrylates oligomer, 2-phenoxy ethyl acrylate, 2-phenoxy ethyl acrylate, Phenol ethoxy rate monoacrylate, 2-(p-chlorophenoxy) ethyl acrylate, p-chlorophenyl acrylate, phenyl acrylate, 2-phenylethyl acrylate, The ether (2-acrylic oxyethyl) of bisphenol A, the ethoxylated bisphenol A diacrylate, 2-(1-naphthyl)oxy ethyl acrylate, o-biphenyl acrylate, o-biphenyl acrylate, a 9,9-bis(4-acryloxy diethoxyphenyl)fluorene, A 9,9-bis(4-acryloxy TORIETOKISHI phenyl)fluorene, A 9,9-bis(4-acryloxy dipropoxyphenyl)fluorene, A 9,9-bis(4-acryloxy ethoxy-3-methylphenyl)fluorene, a 9,9-bis(4-acryloxy ethoxy-3-ethylphenyl)fluorene, a 9,9-bis(4-acryloxy ethoxy-3,5-dimethyl)fluorene, etc. are illustrated.

[0030]

The sulfur content acrylic compound currently indicated by JP,61-72748,A can also be used. For example, 4,4'-bis(beta-acryloyloxyethyl thio)diphenylsulfone, 4,4'-bis(beta-acryloyloxyethyl thio)diphenyl ketone, Although 4,4'-bis(beta-acryloyloxyethyl thio)-3,3',5,5'-tetra bromo diphenyl ketone and 2,4-bis(beta-acryloyloxyethyl thio)diphenyl ketone are mentioned, it is not limited to these.

[0031]

As methacrylic acid ester, the compound in which "acrylate" turns into "methacrylate" among the above-mentioned acrylic ester compound names, "acryloxy" turns into "meta-KURIROKISHI", and "acryloyl" turns into "methacryloyl one" is illustrated as an example.

[0032]

As an optical cationic polymerization nature compound, the cyclic ether, thioether, and vinyl ether which are represented by an epoxy ring and the oxetane ring are mentioned. An epoxy ring content compound is mentioned as an example. Polyalkylene glycol diglycidyl ether, bisphenol A diglycidyl ether, glycerol triglycidyl ether and a jig -- a lycse -- roll triglycidyl ether. Although diglycidyl hexahydro phthalate, trimethylolpropane diglycidyl ether, allyl glycidyl ether, phenyl glycidyl ether, cyclohexane oxide, etc. are illustrated, it is not limited to these.

[0033]

The compound which embellished the metal particle surface with the reactant group can also be used, for example, Ti with a refractive index high as metal particles, Zr, Zn, In, Sn, etc. are illustrated. As a gestalt of photopolymerization, the above-mentioned radical polymerization and cationic polymerization are mentioned. It can introduce by the ethylenic unsaturated double bond in which at least one addition condensation is possible being mentioned as a functional group in which an optical radical polymerization is possible, for example, processing a surface of metal by an ethylenic unsaturated double bond content silane coupling agent etc. As an ethylenic unsaturated double bond content silane coupling agent, although the above-mentioned vinylsilane, an acryloyl (meta) silane, etc. can be used, it is not limited to these.

[0034]

It can introduce by the cyclic ether, thioether, and vinyl ether which are represented by an

epoxy ring and the oxetane ring being mentioned as a functional group in which optical cationic polymerization is possible, for example, processing a surface of metal by an epoxy ring content silane coupling agent. As an epoxy ring content silane coupling agent, although beta-(3, 4-epoxycyclohexyl) ethyltrimethoxysilane, gamma-glycididoxypropytrimethoxysilane, etc. are illustrated, it is not limited to these.

[0035]

(3) Photopolymerization initiator

As a polymerization initiator which constitutes the photosensitive composition for volume type hologram record of this invention, an optical radical polymerization initiator thru/or an optical cationic initiator can be used. The content of these photopolymerization initiators is five to 15 weight section preferably 0.1 to 20 weight section to binder resin in 100 weight section.

[0036]

As an optical radical polymerization initiator, an imidazole derivative, a screw imidazole derivative, N-aryl glycidine derivative, an organic azide compound, titanocene, an aluminumate complex, Organic peroxide, N-alkoxy pyridinium salt, a thioxan ton derivative, etc. are mentioned, and also specifically, 1,3- β l ((t-butylidioxycarbonyl) benzophenone, 3,3',4,4'-tetakis ((t-butylidioxycarbonyl) benzophenone, 3-phenyl-5-iso oxazolone, 2-mercapto benzimidazole, Bis(2,4,5-triphenyl)imidazole, 2,2-dimethoxy-1,2-diphenylethan 1-one (trade name IRGACURE 661, made in Tiba Specialty Chemicals), 1-hydroxy-cyclohexyl-phenyl-ketone (trade name IRGACURE 184, made in Tiba Specialty Chemicals), 2-benzyl-2-dimethylamino 1-(4-morpholinophenyl)- Butanone-1 (trade name IRGACURE 369, made in Tiba Specialty Chemicals), Although bis(eta-5-2,4-cyclopentadiene 1-yl)-bis(2,6-difluoro-3-(1H-pyrrol 1-yl)-phenyl)titanium (trade name IRGACURE 784, made in Tiba Specialty Chemicals) etc. are mentioned, it is not limited to these.

[0037]

As an optical cationic initiator, sulfonic ester, imide sulfonate, Dialkyl 4-hydroxysulfonium salt, aryl sulfone acid-p-nitrobenzyl ester, Although a silanol aluminum complex, iron (eta-eta-6-benzene)5-cyclopentadienyl) (II), etc. are illustrated and also benzoin tosylate, 2,5-dinitrobenzyl tosylate, N-TOSHIFUTARU acid imide, etc. are specifically mentioned, it is not limited to these.

[0038]

As what is used also as an optical cationic initiator also as an optical radical polymerization initiator, Aromatic iodonium salt, aromatic sulfonium salt, aromatic diazonium salt, aromatic phosphonium salt, a triazine compound, an iron arene complex, etc. are illustrated, and also specifically, Diphenyliodonium, ditolyl iodonium, bis(p-tert-butylphenyl)iodonium, Chloride of iodonium, such as bis(p-chlorophenyl)iodonium, Iodonium salt, such as bromide, Howe fluoride salt, a hexafluorophosphate salt, and a hexafluoroantimonate salt, Triphenylsulfonium, 4-tert-

butyl triphenylsulfonium, Chloride of sulfonium, such as tris (4-methylphenyl) sulfonium, sulfonium salt, such as bromide, Howe fluoride salt, a hexafluorophosphate salt, and a hexafluoroantimonate salt, 2,4,6-tris (trichloromethyl)-1,3,5-triazine, 2-phenyl-4,6-bis (trichloromethyl)-1,3,5-triazine, Although 2, such as 2-methyl-4,6-bis(trichloromethyl)-1,3,5-triazine, 4,6-substitution-1, 3, and 5-triazine compound is mentioned, it is not limited to these.

[0039] As for a photopolymerization initiator, it is preferred that decomposition treatment is carried out after hologram recording from a viewpoint of stabilization of the recorded hologram.

(4) Sensitizer

The sensitizer which constitutes the photosensitive composition for volume type hologram record of this invention bears the role to which sensitization of the sensitivity to the recording light of the above-mentioned photopolymerization initiator is carried out. Specifically Thio pyrylium salt dye, merocyanine system coloring matter, quinoxaline dye, Styrylquinoline dye, ketocoumarin dye, thioxanthene dye, a xanthene dye, oxonol dye, cyanine dye, rhodamine dye, pyrylium salt dye, cyclopentanone system coloring matter, cyclohexanone series coloring matter, etc. are illustrated. As an example of cyanine and merocyanine system coloring matter, 3,3'-dicarboxyethyl-2,2'-thiocyaninebromide, 1'-carboxymethyl 2,2'-kino cyaninebromide, 1,3'-diethyl-2,2'-kino thia cyanineiodide, 3-ethyl-5-[(3-ethyl-2(3H)-benzothia ZORIRIDEN) ethylidene]-2-thioxo 4-oxazolidine, etc. are mentioned. As an example of a coumarin and ketocoumarin dye, A 3-(2'-benzimidazole)-7'-diethylamino coumarin, Although a 3,3'-carbonyl screw (7'-diethylamino coumarin), a 3,3'-carbonyl bisque marine **3,3'-carbonyl screw (5',7'-dimethoxycoumarin), a 3,3'-carbonyl screw (7'-acetoxy coumarin), etc. are mentioned, it is not limited to these.

[0041] As for a visible photosensitizer, when high transparency like an optical element is required, what becomes colorlessness by decomposition etc. is preferred at the time of the post process after hologram recording, heating, or UV irradiation.

[0042] The content of this sensitizer is 0.01 to 3 weight section preferably 0.01 to 10 weight section to binder resin 100 weight section.

[0043]

It is made to dissolve in a solvent and these photosensitive compositions for volume type hologram record are used as coating liquid. As a solvent, acetone, methyl ethyl ketone, methyl isobutyl ketone, Cyclohexanone, benzene, toluene, xylene, chlorobenzene, A tetrahydrofuran, methyl cellosolve, ethylcellosolve, methyl-cellosolve acetate, Although **, such as ethylcellosolve acetate, ethyl acetate, 1,4-dioxane, 1,2-dichloroethane, dichloromethane,

chloroform, methanol, ethanol, and isopropanol, are mentioned, it is not limited to these.

[0044]

2. Photosensitive medium for volume type hologram record

Next, the photosensitive medium for volume type hologram record using the above-mentioned constituent for volume type hologram record is explained.

[0045]

The photosensitive medium for volume type hologram record in this invention provides the photosensitive layer which consists of the above-mentioned constituent on a transparent base material.

The volume hologram characteristic after exposure changes with character of the binder resin which constitutes the constituent.

[0046]

Namely, the case where average molecular weights are 10,000-250,000, and glass transition temperature uses a not less than 80 °* acrylic resin as binder resin, and an average molecular weight by 300,000-1 million. And when glass transition temperature uses vinyl acetate system resin 60 °* or less, the half breadth of a diffraction spectrum is 20 nm or less, and the amount of refractive index modulation of the hologram after volume hologram record is 0.03 or more.

On the other hand, when average molecular weights are 10,000-260,000 and glass transition temperature uses vinyl acetate system resin 60 °* or less as binder resin, the half breadth of a diffraction spectrum is not less than 25 nm, and the amount of refractive index modulation is 0.03 or more.

[0047]

The photosensitive medium for volume type hologram record applies on a substrate the coating liquid which consists of the above-mentioned constituent using a spin coater, a photogravure coating machine, a comma coating machine, or a bar coating machine, and it dries and it is obtained by forming a photosensitive layer.

[0048]

As a substrate used for the photosensitive medium for volume type hologram record, What is necessary is just transparency resin etc. which it has, and A polyethylene film, a polypropylene film, A polychloroethylene system film, a polyvinylidene fluoride film, a polyvinylchloride film, A polyvinylidene chloride film, an ethylene-vinyl alcohol film, A polyvinyl alcohol film, a polymethylmethacrylate film, A polyether sulfone film, a polyether ether ketone film, Resin, such as polyester film, such as a polyamide film, a tetrafluoroethylene perfluoroalkyl vinyl ether copolymerization film, and a polyethylene terephthalate film, and a polyimide film, is mentioned.

[0049]

As thickness of this substrate, 2-200 micrometers is 10-50 micrometers preferably. As for especially the coverage of the above-mentioned constituent, it is preferred that 1-100 micrometers of thickness of this coating film after spreading desiccation are set to 10-40 micrometers. When the coating film after desiccation has adhesiveness, this film can be laminated on a spreading side using the film illustrated as the above-mentioned substrate as a protective film. In this case, releasing treatment may be carried out so that it may be easy to remove the contact surface of a laminate film and a spreading side afterwards.

[0050]

3. Record method of volume hologram

In record of a hologram, they are visible laser beams (458 nm), for example, an Ar ion laser. It is recordable on the photosensitive medium for volume type hologram record using laser beams, such as 488 nm, 514.5 nm, krypton ion laser (647.1 nm), helium neon ion laser (632 nm), and an YAG laser (532 nm).

[0051]

As a method of recording a volume type hologram on the photosensitive medium for volume type hologram record, which method of being known from the former may be used.

[0052]

For example, the original edition is stuck in the hologram recording material layer of the photosensitive medium for volume type hologram record, and a volume type hologram is recorded by performing interference exposure using ionizing radiation like visible light or ultraviolet radiation, or an electron beam from the transparent substrate film side.

[0053]

Full exposure, heating, etc. by ultraviolet rays can be suitably processed after interference exposure for promotion of refractive index modulation, and a polymerization reaction conclusion.

[0054]

Thus, in the obtained volume type hologram, a diffraction spectrum can be obtained by measuring a transmissivity spectrum using publicly known art. "Half breadth" Γ in this invention] The becoming term means the spectral band width in the value of $(T_p^b - T_p^d) / 2$ at the time of making transmissivity of T_p and a peak value into T_p^d for the transmissivity of the baseline of this diffraction spectrum in the wavelength which shows a diffraction peak.

[Work example 1]

[0055]

Example 1

The photosensitive composition solution for volume type hologram record was adjusted using the material shown below.

[0056]

Polymethacrylate
(Polystyrene equivalent-weight average molecular weight: 15,000) 100 weight sections

1, 6-hexanediol diglycidyl ether

(Nagase Chemtex EX-212) 70 weight sections

Diphenoxyethanol fluorene diacrylate

(Osaka Gas BPFA) 80 weight sections

Diaryliodonium salt (product made from low DIA, P12074) 5 weight section

2,5-bis-(4-diethylamino benzyl) cyclopentanone 1 weight section

1-butanol 30 weight section

Methyl-ethyl-ketone 30 weight section

The bar coating machine was used on a 38-micrometer polyethylene terephthalate (PET) film (Toray Industries Iumler T-60), the adjusted above-mentioned solution was applied so that it might become 10 micrometers of dry membrane thickness, and the photosensitive medium for volume type hologram record was produced.

The photosensitive layer side was laminated to the mirror, a 532-nm laser beam was 60-

mJ/cm²-entered from the PET side, and the volume type hologram was recorded.

[0057]

Subsequently, the photosensitive layer was fixed by heating and ultraviolet-rays complete

exposure, and the volume type hologram was obtained.

About the obtained volume hologram, transmissometry of the spectrophotometer (Shimadzu UVPC-3100) was performed and calculation of the amount of refractive index modulation

(delta n), diffraction efficiency, and half breadth was performed.

[0058]

The diffraction efficiency eta makes transmissivity of T_p and a baseline T_b for the peak

transmittance of the obtained transmission spectrum, and is a following formula,

$$\eta = (T_p - T_b) / T_p$$

It is alike, and computes more and half breadth (T_{1/2}) is a following formula about the peak

value (T_p) of transmissivity, and one half of the values of the difference of baseline

transmissivity (T_p),

$$T_{1/2} = (T_p - T_b) / 2$$

It was alike, and computed more and transmission-spectrum (transmitted wave length) width at the time of T_{1/2} was made into half breadth. delta n was computed with the above-mentioned

Kogelnik theoretical formula using the value of the diffraction efficiency and half breadth which

were obtained.

[0059]

Example 2

The photosensitive composition solution for volume type hologram record was adjusted using the material shown below.

Polyethylmethacrylate

(Polystyrene equivalent-weight average molecular weight: 70,000) 100 weight sections

1, 6-hexanediol diglycidyl ether

(Nagase Chemtex EX-212) 70 weight sections

Diphenoxylethanol fluorene diacrylate

(Osaka Gas BPFA) 80 weight sections

Diazliodonium salt (product made from low DIA, PI2074) 5 weight section

2,5-bis-(4-diethylamino benzylidene) cyclopentanone 1 weight section

1-butanol 30 weight section

Methyl-ethyl-ketone 30 weight section

Like Example 1, volume type hologram production was carried out and measurement about various physical properties was performed.

[0060]

Example 3

The photosensitive composition solution for volume type hologram record was adjusted using the material shown below.

Polyethylmethacrylate

(Polystyrene equivalent-weight average molecular weight: 93,000) 100 weight sections

1, 6-hexanediol diglycidyl ether

(Nagase Chemtex EX-212) 70 weight sections

Diphenoxylethanol fluorene diacrylate

(Osaka Gas BPFA) 80 weight sections

Diazliodonium salt (product made from low DIA, PI2074) 5 weight section

2,5-bis-(4-diethylamino benzylidene) cyclopentanone 1 weight section

1-butanol 30 weight section

Methyl-ethyl-ketone 30 weight section

Like Example 1, volume type hologram production was carried out and measurement about various physical properties was performed.

[0061]

Example 4

The photosensitive composition solution for volume type hologram record was adjusted using the material shown below.

Polyethylmethacrylate

(Polystyrene equivalent-weight average molecular weight: 120,000) 100 weight sections

1, 6-hexanediol diglycidyl ether
(Nagase Chemtex EX-212) 70 weight sections
Diphenoxyethanol fluorene diacrylate
(Osaka Gas BPFFA) 80 weight sections
Diaryliodonium salt (product made from low DIA, P12074) 5 weight section
2,5-bis-(4-diethylamino benzyliene) cyclopentanone 1 weight section
1-butanol 30 weight section
Methyl-ethyl-ketone 30 weight section
Like Example 1, volume type hologram production was carried out and measurement about various physical properties was performed.

[0062]

Example 5

The photosensitive composition solution for volume type hologram record was adjusted using the material shown below.

Polyvinyl acetate
(Polystyrene equivalent-weight average molecular weight: 500,000) 100 weight sections
1, 6-hexanediol diglycidyl ether
(Nagase Chemtex EX-212) 70 weight sections
Diphenoxyethanol fluorene diacrylate
(Osaka Gas BPFFA) 80 weight sections

Diaryliodonium salt (product made from low DIA, P12074) 5 weight section
2,5-bis-(4-diethylamino benzyliene) cyclopentanone 1 weight section

1-butanol 30 weight section

Methyl-ethyl-ketone 30 weight section

Like Example 1, volume type hologram production was carried out and measurement about various physical properties was performed.

[0063]

Example 6

The photosensitive composition solution for volume type hologram record was adjusted using the material shown below.

Polyvinyl acetate
(Polystyrene equivalent-weight average molecular weight: 83,000) 100 weight sections
1, 6-hexanediol diglycidyl ether
(Nagase Chemtex EX-212) 70 weight sections
Diphenoxyethanol fluorene diacrylate
(Osaka Gas BPFFA) 80 weight sections

Diaryliodonium salt (product made from low DIA, P12074) 5 weight section

2,5-bis-(4-diethylamino benzylidene) cyclopentanone 1 weight section

1-butanol 30 weight section

Methyl-ethyl-ketone 30 weight section

Like Example 1, volume type hologram production was carried out and measurement about

[0064]

Example 7

The photosensitive composition solution for volume type hologram record was adjusted using

the material shown below.

Polyvinyl acetate

(Polystyrene equivalent-weight average molecular weight: 100,000) 100 weight sections

1, 6-hexanediol diglycidyl ether

(Nagase Chemtex EX-212) 70 weight sections

Diphenoxyethanol fluorene diacrylate

(Osaka Gas BPFFA) 80 weight sections

Diarylodonium salt (product made from low DIA, P12074) 5 weight section

2,5-bis-(4-diethylamino benzylidene) cyclopentanone 1 weight section

1-butanol 30 weight section

Methyl-ethyl-ketone 30 weight section

Like Example 1, volume type hologram production was carried out and measurement about

various physical properties was performed.

[0065]

Example 8

The photosensitive composition solution for volume type hologram record was adjusted using

the material shown below.

Polyvinyl acetate

(Polystyrene equivalent-weight average molecular weight: 260,000) 100 weight sections

1, 6-hexanediol diglycidyl ether

(Nagase Chemtex EX-212) 70 weight sections

Diphenoxyethanol fluorene diacrylate

(Osaka Gas BPFFA) 80 weight sections

Diarylodonium salt (product made from low DIA, P12074) 5 weight section

2,5-bis-(4-diethylamino benzylidene) cyclopentanone 1 weight section

1-butanol 30 weight section

Methyl-ethyl-ketone 30 weight section

Like Example 1, volume type hologram production was carried out and measurement about

various physical properties was performed.

[0066]

Example 9

The photosensitive composition solution for volume type hologram record was adjusted using the material shown below.

Polyvinyl acetate

(Polystyrene equivalent-weight average molecular weight: 170,000) 100 weight sections

1, 6-hexanediol diglycidyl ether

(Nagase Chemtex EX-212) 70 weight sections

Diphenoxethanol fluorene diacrylate

(Osaka Gas BPFEA) 80 weight sections

Diallyliodonium salt (product made from low DIA, PI2074) 5 weight section

2,5-bis-(4-diethylamino benzylidene) cyclopentanone 1 weight section

1-butanol 30 weight section

Methyl-ethyl-ketone 30 weight section

Like Example 1, volume type hologram production was carried out and measurement about various physical properties was performed.

[0067]

Example 10

The photosensitive composition solution for volume type hologram record was adjusted using the material shown below.

Polyethylacrylate

(Polystyrene equivalent-weight average molecular weight: 100,000) 100 weight sections

1, 6-hexanediol diglycidyl ether

(Nagase Chemtex EX-212) 70 weight sections

Diphenoxethanol fluorene diacrylate

(Osaka Gas BPFEA) 80 weight sections

Diallyliodonium salt (product made from low DIA, PI2074) 5 weight section

2,5-bis-(4-diethylamino benzylidene) cyclopentanone 1 weight section

1-butanol 30 weight section

Methyl-ethyl-ketone 30 weight section

Like Example 1, volume type hologram production was carried out and measurement about various physical properties was performed.

[0068]

Comparative example 1

The photosensitive composition solution for volume type hologram record was adjusted using the material shown below.

Polyethylmethacrylate

(Polystyrene equivalent-weight average molecular weight: 120,000) 100 weight sections 1, 6-hexanediol diglycidyl ether (Nagase Chemtex EX-212) 70 weight sections Diphenoxxyethanol fluorene diacrylate (Osaka Gas BPFA) 80 weight sections 2-mercaptopbenzothiazole (made by Aldrich) 5 weight section 2,5-dinitrobenzyl tosylate 5 weight section 4,5-bis-(4-diethylamino benzylidene) cyclopentanone 1 weight section 1-butanol 30 weight section Methyl-ethyl-ketone 30 weight section Like Example 1, volume type hologram production was carried out and measurement about various physical properties was performed. The material physical properties of the used binder resin and the evaluation result of a volume hologram are shown in Table 1.

[table 1]

表 1 バイナリ樹脂の材料物性および体積ホログラムの評価結果

| 樹脂 | Tg (°C) | 分子重* | Δn | 回折効率 (%) | 半値幅 (mm) | 評価 | |
|--------|---------|---------|-------|----------|----------|----|--|
| | | | | | | | |
| 実施例 1 | 98 | 15,000 | 0.031 | 60 | 20 | | |
| 実施例 2 | 105 | 70,000 | 0.035 | 90 | 18 | | |
| 実施例 3 | 110 | 93,000 | 0.034 | 93 | 17 | | |
| 実施例 4 | 114 | 120,000 | 0.031 | 95 | 15 | | |
| 実施例 5 | 45 | 500,000 | 0.032 | 80 | 18 | | |
| 実施例 6 | 43 | 83,000 | 0.050 | 70 | 30 | | |
| 実施例 7 | 45 | 100,000 | 0.047 | 80 | 28 | | |
| 実施例 8 | 30 | 260,000 | 0.044 | 76 | 25 | | |
| 実施例 9 | 45 | 170,000 | 0.050 | 84 | 27 | | |
| 実施例 10 | -24 | 100,000 | 0.065 | 74 | 38 | | |
| 比較例 1 | | 300,000 | 0.029 | 98 | 13.6 | | |

* ポリマチル平均分子量

[translation done.]